

# **Influence of Gaseous Atmosphere on Electrochemical Behavior of Nickel**

## **Alloys in LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> at 700 °C**

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### **KEYWORDS**

A. Molten salts; A. Nickel; B. Polarization; B. SEM; C. High temperature corrosion; C. Hot corrosion

## ABSTRACT

Electrochemical behavior of Ni alloys (Ni,  $\beta$ -NiAl,  $\beta$ -NiAl/Cr) was investigated in LiCl-KCl- $\text{Na}_2\text{SO}_4$  electrolyte at 700 °C under three gaseous atmospheres (Ar,  $\text{O}_2$ ,  $\text{O}_2$ -0.1% $\text{SO}_2$ ). In oxidizing atmospheres, Ni rapidly degraded due to instability of NiO, and alumina-rich scale on  $\beta$ -NiAl provided limited protection against hot corrosion (e.g., cracks in the scale under  $\text{O}_2$ -0.1% $\text{SO}_2$ ); however, the addition of both Al and Cr resulted in enhanced corrosion resistance by forming a mixed-oxide ( $\text{Al}_2\text{O}_3$ - $\text{Cr}_2\text{O}_3$ ) scale in oxidizing atmospheres. In hot corrosion processes of Ni alloys, the formation and stability of oxide scales in the molten salt were influenced by gaseous atmosphere and alloying elements.

## 1. INTRODUCTION

Nickel alloys are widely employed as constructional or coating materials for high temperature applications (e.g., gas turbines or fossil fuel power plants) requiring both oxidation and corrosion resistance. Aggressive chemical and thermal environments found in gas turbines are well known to accelerate the degradation of these alloys in hot section components [1–3]. For example, sulfate-containing salt deposits (e.g., NaCl-Na<sub>2</sub>SO<sub>4</sub>) from combustion of high sulfur-content fuel and ingestion of polluted air accelerate the degradation of Ni alloys at elevated temperatures (650–1000 °C)—hot corrosion [1,4].

The degradation modes of hot corrosion are often classified as high-temperature (Type I) hot corrosion (e.g., 900–1000 °C) and low-temperature (Type II) hot corrosion (e.g., 650–750 °C). This classification was made primarily based on the accelerated corrosion rates observed at these two temperature ranges, due to the formation of liquid-state salt deposits [5–8]. Based on sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) which melts at 884 °C, molten Na<sub>2</sub>SO<sub>4</sub> (Type I, 900–1000 °C) deposits were found to accelerate the degradation of Ni alloys under oxidizing atmospheres, especially in the presence of SO<sub>3</sub> [6,9]. The reaction rate of Ni with Na<sub>2</sub>SO<sub>4</sub> is expected to decrease at lower temperatures (Type II, 650–750 °C) as Na<sub>2</sub>SO<sub>4</sub> is initially solid; however, the degradation rate of Ni was also accelerated in SO<sub>3</sub>-containing atmosphere as NiO reacted with SO<sub>3</sub> molecules to form nickel sulfate (NiSO<sub>4</sub>), resulting in a molten sulfate solution (Na<sub>2</sub>SO<sub>4</sub>-NiSO<sub>4</sub>,  $T_{\text{eutectic}} = 670$  °C) [6,7].

A number of studies on sulfate-induced hot corrosion identified a variety of degradation reaction pathways, including sulfidation, formation of transition metal sulfates (NiSO<sub>4</sub> or CoSO<sub>4</sub>), as well as dissolution of metal oxides (e.g., NiO, Al<sub>2</sub>O<sub>3</sub>, and Cr<sub>2</sub>O<sub>3</sub>) in the salt deposit (fluxing mechanisms) [10–13], all of which were influenced by gaseous atmosphere (e.g., O<sub>2</sub>, O<sub>2</sub>-SO<sub>2</sub>-SO<sub>3</sub>).

In selecting Ni alloys to mitigate hot corrosion reactions, oxygen-active elements (Al and Cr) are critical constituents due to their capability to form protective oxide scales at elevated temperatures [14–16].

In both types of hot corrosion processes, the presence of sulfate-containing molten salts is the essential factor in accelerating the degradation reaction of Ni alloys by providing chemically aggressive ionic solutions (electrolytes), suggesting the utility of electrochemical corrosion testing of Ni alloys (electrodes) in understanding and evaluating their degradation behavior in addition to more popular approaches of coupon exposure and burner-rig tests [17]. This work specifically studied the sulfate-induced hot corrosion behavior of three Ni alloys (Ni,  $\beta$ -NiAl at 50-50 mol%, and  $\beta$ -NiAl/Cr at 47.5-47.5-5 mol%), using electrochemical open-circuit potential and potentiodynamic polarization techniques in molten LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> (53.3-36.7-10 mol%) solution at 700 °C. Due to the importance of gaseous atmosphere in hot corrosion processes [1,2,7,18], the electrochemical corrosion testing was conducted under the control of gaseous atmosphere: from inert argon to pure O<sub>2</sub> and to O<sub>2</sub>-0.1%SO<sub>2</sub> gas mixture.

Overall, electrochemical corrosion measurements in this work aimed to elucidate the effects of gaseous atmosphere and oxygen-active elements (Al and Cr) in hot corrosion processes by comparing the stability of oxide scales from each alloy in the molten salt (e.g., NiO scale from Ni). The electrochemical corrosion behavior of Ni alloys was corroborated with the results from immersion tests in the same environment by characterizing the chemistry and microstructure of corrosion scales. The morphologies of the corrosion layers and degradation reactions were discussed within the context of prior hot corrosion studies in the literature under similar environmental conditions.

## **2. EXPERIMENTAL**

## 2.1 Electrochemical cell components for corrosion testing

*Bulk electrolyte:* Sulfate-containing bulk electrolyte, LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> (53.3-36.7-10 mol%), was prepared from appropriate weights of lithium chloride (anhydrous, 99.0%, Alfa Aesar, product # 10515), potassium chloride (KCl, 99.0%, Sigma Aldrich, product # 746436), and sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>, 99.0%, Sigma Aldrich, product # 238597) inside an argon filled glovebox (O<sub>2</sub> and H<sub>2</sub>O < 0.5 ppm) due to the hygroscopic nature of salts. Weighed salts were contained in a plastic bottle (500 mL) and mixed together by manually shaking the bottle. About 70 g of the bulk electrolyte mixture was poured into an alumina crucible (5.4 cm inner in diameter and 11 cm in height) for electrochemical cell assembly.

*Electrodes:* The alloy working electrodes (WEs) of pure Ni,  $\beta$ -NiAl (50-50 mol%), and  $\beta$ -NiAl/Cr (47.5-47.5-5 mol%) were prepared from pure metals of Ni wire (99.5%, 1 mm in diameter, Alfa Aesar, product # 41361), Al wire (99.0%, 1 mm in diameter, Alfa Aesar, product # 11064), and Cr pieces (99.995%, Alfa Aesar, product # 38494) using an arc-melter (MAM1, Edmund Buhler GmbH). Homogeneous alloys were fabricated in the form of cylindrical rods (0.3 cm in diameter and 3.0 cm in length) by suction casting in a copper mold. The arc-melted alloy rods were annealed at 1100 °C for 24 h under vacuum (< 5 mtorr) to stabilize their microstructures, and the alloy surface was polished using silicon carbide emery papers (up to 1200 grit) to remove surface oxides produced during the alloy fabrication. The alloy WEs were electrically connected to stainless steel rods (3.2 mm in diameter and 46 cm in length) with the connection established above the electrolyte in order to avoid the direct contact between the electrical leads and the molten salts during electrochemical measurements. Pure Ni WEs were connected to stainless steel rods via stainless steel adapters using 5-40 threads; the brittle  $\beta$ -NiAl and  $\beta$ -NiAl/Cr alloy WEs were

directly tied to stainless steel rods using Ni-Cr (78-22 mol%) wire (0.25 mm in diameter), as shown in Figure 1a.

**[Figure 1]**

The Ag/Ag<sup>+</sup> reference electrode (RE) was constructed using a closed one-end mullite tube (6.4 mm in outer diameter, 4.8 mm in inner diameter, and 45.7 cm in length) which contained ~1.0 g of LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub>-Ag<sub>2</sub>SO<sub>4</sub> reference electrolyte and Ag wire (1 mm in diameter and 48 cm in length) to establish the Ag/Ag<sup>+</sup> half-reaction (Figure 1a). The reference electrolyte, LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub>-Ag<sub>2</sub>SO<sub>4</sub> (48-33-9-10 mol%), was prepared by adding 10 mol% of Ag<sub>2</sub>SO<sub>4</sub> (99.999%, Sigma Aldrich, product # 204412) into the bulk electrolyte composition. The electrolyte mixture was placed in a quartz crucible (24 mm in inner diameter and 14 cm in length) for premelting in a stainless steel vacuum chamber. The chamber was loaded into a crucible furnace (Mellen, CC-12), evacuated to less than 5 mtorr, and heated under vacuum at 80 °C for 12 h and at 230 °C for 12 h to remove residual moisture. Then, the chamber was purged with ultra-high purity argon three times, heated at 700 °C for 3 h for premelting, and cooled to room temperature under flowing argon. In an argon-filled glovebox, the dry and homogeneous reference electrolyte was crushed into a fine power, the powder was poured into the mullite tube with Ag wire inserted, and the open-end of the mullite tube was sealed using epoxy.

A graphite rod (0.95 cm in diameter and 1 cm in length) was used as the counter electrode (CE), female threaded at the top and electrically connected to a male threaded steel rod (3.2 mm in diameter and 46 cm in length) via 5-40 threads (Figure 1a). The entire graphite CE was immersed in the molten salt during experiments to prevent the direct contact with oxidizing atmospheres, thus avoiding the rapid oxidation (or consumption) of the graphite (CO or CO<sub>2</sub>). The stainless steel rod above the graphite CE was sheathed with a threaded boron nitride (BN) tube

(6.35 mm in outer diameter, 3.2 mm in inner diameter, and 1.5 cm in length) in order to minimize its direct exposure to the corrosive bulk electrolyte during the electrochemical measurements.

## **2.2 Electrochemical cell assembly and measurements**

*Cell assembly:* Electrochemical corrosion testing of Ni alloys was conducted in a closed one-end alumina test chamber (10.5 cm in inner diameter, 11.4 cm in outer diameter, and 43 cm in length, Coorstek). The chamber was capped with a stainless steel flange (QF100-BF, Kurt J. Lesker) where seven ultra-torr fittings (6.35 mm in inner diameter, Swagelok) were installed to insert electrical leads and a K-type thermocouple (Figure 1b). The alumina crucible filled with the bulk electrolyte (~70 g) was placed inside the test chamber, on the flat surface established with alumina powder. Two of each WE, RE, and CE were inserted through vacuum fittings of the cap until each electrode touched the bottom of the alumina crucible with the configuration shown in Figure 1b. Electrical leads for WEs and CEs were electrically isolated from the stainless steel flange using quartz tubing (6.35 mm in outer diameter, 4.0 mm in inner diameter, and 15 cm in length) and the top end of the tube was sealed using epoxy. The K-type thermocouple was placed in the electrolyte, but was enclosed by a closed one-end quartz tube (46 cm in length) to avoid direct contact of the thermocouple sheath (stainless steel) with the corrosive electrolyte at 700 °C. The test chamber was sealed using a silicone O-ring between the test chamber and the flange.

The assembled test chamber (Figure 1b) was loaded into a vertical crucible furnace, evacuated to less than 5 mtorr, and heated under vacuum at 80 °C for 12 h and at 230 °C for 12 h to remove moisture from the cell components and the electrolyte mixture. Then, the chamber was purged with ultra-high purity argon three times, heated to 700 °C under flowing argon (~50 mL/min), and the cell temperature was recorded using a thermocouple data acquisition board (NI 9211, National Instruments). Under inert argon, the electrochemical cell was allowed to equilibrate

until the cell temperature reached a steady temperature at 700 °C ( $\pm 4$  °C) and until the potential difference between the two identical REs was less than 5 mV to ensure reliable electrochemical measurements.

*Electrochemical measurements:* Once the cell reached the steady temperature at 700 °C and RE stability within 5 mV difference under inert argon, the electrodes were connected to a potentiostat-galvanostat (PGSTAT 302F, Metrohm) for electrochemical measurements using a three-electrode cell configuration (graphite CE and Ag/Ag<sup>+</sup> RE). For experiments under oxidizing atmospheres, pure O<sub>2</sub> gas (Praxair) or O<sub>2</sub>-0.1%SO<sub>2</sub> gas mixture (Praxair, OX SD1000C-AS) was introduced into the test chamber at the flow rate of ~50 mL/min, and the open-circuit potentials of the alloy WEs were measured for about 12 h. In the case of experiments under O<sub>2</sub>-0.1%SO<sub>2</sub> atmosphere, a platinum mesh (2.5 cm  $\times$  2.5 cm) was rolled and inserted into the gas inlet tube near the top of the alumina crucible (Figure 1b) in order to establish equilibrium partial pressure of SO<sub>3</sub> at 700 °C by facilitating the following reaction:



The equilibrium partial pressure of SO<sub>3</sub> ( $P_{\text{SO}_3}$ ) in O<sub>2</sub>-0.1%SO<sub>2</sub> was estimated to be  $7 \times 10^{-4}$  atm from the above reaction at 700 °C [19].

Following open-circuit potential measurement for 12 h, the alloy WE was subjected to potentiodynamic polarization and the current response was measured in each gaseous atmosphere. The electrode potential ( $E$ ) of each WE was initially applied at 0.05 V more negative than the open-circuit potential ( $E_{\text{OCP}}$ ), swept in the anodic (positive) direction at a scan rate of 1 mV/s, and terminated at 0.50 V more positive than the open-circuit potential. Upon completion of electrochemical measurements, the alloy WEs were raised above the bulk electrolyte solution, the cell was cooled to room temperature, and the immersion depth of alloy WEs was measured. Based

on the immersion depth (1.6 cm) of the alloy WEs in the electrolyte, the exposed surface area was estimated to be 1.58 cm<sup>2</sup>. The current density ( $j$ ) of each electrode, based on exposed surface area, was obtained as a function of overpotential  $\eta$  ( $= E - E_{\text{OCP}}$ ) over  $-0.05 \text{ V} < \eta < 0.50 \text{ V}$  and the polarization curve ( $\log |j|$  vs.  $\eta$ ) was plotted and analyzed.

### **2.3 Immersion tests and characterization of corrosion layer**

In separate experiments using an equivalent set-up in Figure 1, the alloys of pure Ni,  $\beta$ -NiAl, and  $\beta$ -NiAl/Cr were immersed in the LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> electrolyte at 700 °C for 12 h in each gaseous atmosphere. After 12 h immersion, the alloy samples were raised above the electrolyte under argon atmosphere, the test chamber was cooled to room temperature, and the test samples were detached for characterization. Diffraction patterns were obtained from the surface of each alloy sample by X-ray diffractometer (XRD, PANalytical Empyrean) over  $2\theta$  angles of 20–70° for phase identification. In order to characterize the corrosion layer, the tested alloy samples were cut and mounted using epoxy resin and hardener (Allied High Tech Products) at the ratio of 12:1 for metallographic sample preparation. The samples were ground up to 2000 grit using silicon carbide abrasive papers and polished with diamond powder (6–1  $\mu\text{m}$ ) dispersed in ethylene glycol. The polished samples were sputter-coated with gold at ~10 nm thickness and characterized using scanning electron microscopy (SEM, FEI Quanta 200) fitted with energy dispersive spectroscopy (EDS).

## **3. RESULTS AND DISCUSSION**

### **3.1. Electrochemical behavior and the corrosion scale of pure Ni**

Under inert argon, the open-circuit potential ( $E_{\text{OCP}}$ ) of pure Ni electrode was initially at about  $-0.65 \text{ V}$  (vs.  $\text{Ag}/\text{Ag}^+$ ) and reached steady state at  $-0.73 \text{ V}$  (vs.  $\text{Ag}/\text{Ag}^+$ ) (Figure 2a). In contrast, the transition from inert argon to oxidizing atmospheres resulted in a large shift in  $E_{\text{OCP}}$

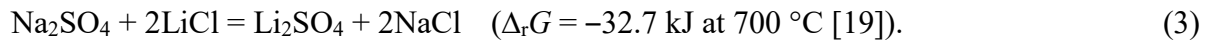
in the opposite direction:  $E_{\text{OCP}} = -0.25 \text{ V}$  (vs.  $\text{Ag}/\text{Ag}^+$ ) in pure  $\text{O}_2$ , and  $E_{\text{OCP}} = -0.29 \text{ V}$  (vs.  $\text{Ag}/\text{Ag}^+$ ) in  $\text{O}_2$ -0.1% $\text{SO}_2$  after 12 h. Such a rapid rise in  $E_{\text{OCP}}$  could be attributed to the presence of strong oxidants ( $\text{O}_2$ ,  $\text{SO}_2$ , and  $\text{SO}_3$ ) in the electrolyte [18], which also resulted in a large increase in current during anodic polarization (Figure 2b), indicating accelerated corrosion rate of Ni under oxidizing atmospheres. Compared to the lowest anodic currents obtained under inert argon, the anodic currents increased by 25–45 times in oxidizing atmospheres of both pure  $\text{O}_2$  and  $\text{O}_2$ -0.1% $\text{SO}_2$ .

### [Figure 2]

Electrochemical behavior of Ni under each gaseous atmosphere was well correlated with the results from immersion testing (Figure 3): the formation of uniform NiO scale under inert argon led to low anodic currents, and non-uniform corrosion scales under oxidizing atmospheres led to increased anodic currents. The corrosion scale thickness drastically changed from 5  $\mu\text{m}$  in argon to  $\sim 374 \mu\text{m}$  in pure  $\text{O}_2$  and  $\sim 143 \mu\text{m}$  in  $\text{O}_2$ -0.1% $\text{SO}_2$ , indicating a rapid corrosion rate of Ni under oxidizing atmospheres. Under inert argon, phase constituents in the corrosion scale included NiO and  $\text{Ni}_3\text{S}_2$ , evidenced by X-ray elemental mapping (Figure 3a) and XRD (Figure 3d), suggesting the reaction of Ni metal with the sulfate ions:



Under oxidizing atmospheres, diffraction peaks of NiO were evident, but stronger peaks were obtained from the electrolyte phase comprised of KCl, NaCl, and  $\text{Li}_2\text{SO}_4$  (Figure 3d) [20–22]. Diffraction peaks of  $\text{Li}_2\text{SO}_4$  and NaCl, instead of  $\text{Na}_2\text{SO}_4$  and LiCl, were observed due to the metathesis reaction in the electrolyte:



### [Figure 3]

The change from argon to pure O<sub>2</sub> atmosphere resulted in the dispersed NiO phase in the electrolyte and the formation of nickel sulfide layer at the metal-scale interface (Figure 3b). In pure O<sub>2</sub>, the formation of NiO would be facilitated by the direct reaction with oxygen:



However, the accelerated dissolution of NiO in pure O<sub>2</sub> was evident, compared to inert argon atmosphere, and is thought to originate from the following reaction (basic dissolution):

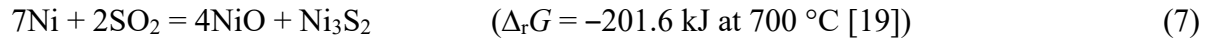


, where the increase in oxygen partial pressure ( $P_{\text{O}_2}$ ) leads to the dissolution of NiO into  $\text{NiO}_2^-$  according to Le Chatelier's principle. The dissolution of NiO can be sustained by exposing the Ni metal surface to the electrolyte and thus, allowing the continued formation of NiO (reactions (2) and (4)) and nickel sulfide (reaction (2)). The dissolution mechanism of NiO in reaction (5) was rationalized based on the measured solubility of NiO in Na<sub>2</sub>SO<sub>4</sub> as a function of the activity of Na<sub>2</sub>O ( $a_{\text{Na}_2\text{O}}$ ) at 927 °C and 1 atm O<sub>2</sub> by Gupta and Rapp [10]. The degradation morphology in this work (Figure 3b) is qualitatively similar to that from isothermal testing of Ni coated with Na<sub>2</sub>SO<sub>4</sub> at 1000 °C in air by Goebel and Pettit [9], including a porous NiO scale mixed with Na<sub>2</sub>SO<sub>4</sub> and a nickel sulfide layer at the metal-oxide interface. They also proposed basic dissolution reactions of NiO according to reaction (5) and the following reaction:



; however, more recent thermodynamic studies suggest that Na<sub>2</sub>NiO<sub>2</sub> is an unstable compound with respect to NiO and Na<sub>2</sub>O above 627 °C [23,24]. Thus, the extensive dissolution of NiO under high  $P_{\text{O}_2}$  (1 atm) compared to inert argon atmosphere is likely to be dominated by reaction (5) considering the thermodynamic instability of Na<sub>2</sub>NiO<sub>2</sub> in reaction (6).

The addition of 0.1%SO<sub>2</sub> in O<sub>2</sub> resulted in a complex corrosion scale comprised of several sub-layers (Figure 3c): (i) top layer enriched with NiO and nickel sulfides, (ii) electrolyte-rich middle layer which included globular nickel sulfides and dissolved Ni ions (see X-ray mapping of Ni in Figure 3c), and (iii) nickel sulfide layer at the metal-scale interface. The presence of nickel sulfides in the scale was the most prominent in O<sub>2</sub>-0.1%SO<sub>2</sub>, possibly due to the reaction of Ni with SO<sub>2</sub> or SO<sub>3</sub>, for example,



, where the increase in  $P_{\text{SO}_2}$  would shift the reaction to the right and increase the rate of nickel sulfide formation. A similar reaction can also be found for SO<sub>3</sub> from reaction (2) by incorporating the following dissociation equilibrium reaction:



While the presence of nickel sulfides was evident from SEM-EDS analysis, the diffraction peaks related to nickel sulfides (e.g., Ni<sub>3</sub>S<sub>2</sub>) were not detected (Figure 3d), possibly due to the formation of complex, off-stoichiometric nickel sulfides. The globular shape of nickel sulfides in the middle layer indicates that nickel sulfides could be in the liquid state at 700 °C. Based on the eutectic temperature (637 °C) and composition (~34 mol% S) from the binary Ni-S phase diagram [25], the formation of liquid-state nickel sulfides at 700 °C is reasonable and supports the possibility of forming off-stoichiometric nickel sulfides away from the Ni<sub>3</sub>S<sub>2</sub> phase.

Furthermore, the partial pressure of SO<sub>3</sub> in O<sub>2</sub>-0.1%SO<sub>2</sub> ( $P_{\text{SO}_3} = 7 \times 10^{-4}$  atm at 700 °C) is well known to accelerate the dissolution of NiO into molten sulfate solution [7]:



, suggesting that high  $P_{\text{SO}_3}$  changes the dissolution mechanism of NiO from basic dissolution (reaction (5) in argon and pure O<sub>2</sub>) to acidic dissolution (reaction (9) in O<sub>2</sub>-0.1%SO<sub>2</sub>). The

accelerated dissolution of NiO into the molten salt under O<sub>2</sub>-0.1%SO<sub>2</sub> atmosphere is supported by the presence of Ni ions in the electrolyte-rich middle layer (Figure 3c).

Overall, the corrosion behavior of Ni in molten LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> was highly dependent upon the gaseous atmosphere which drastically affected the stability of NiO scale through the dissolution and/or formation of nickel oxides, sulfides, and sulfates. In the case of the uniform NiO layer in inert argon, the anodic currents during polarization could be related to the following anodic half-reactions:



; however, in oxidizing atmospheres, far more complex anodic half-reactions are expected to occur due to the presence of additional degradation reaction pathways involving nickel sulfides and sulfates.

### 3.2 Electrochemical behavior and the corrosion scale of $\beta$ -NiAl alloy

The electrochemical corrosion behavior of oxidation-resistant  $\beta$ -NiAl alloy was studied in the same electrolyte (Figure 4) under three gaseous atmospheres (argon, pure O<sub>2</sub>, and O<sub>2</sub>-0.1%SO<sub>2</sub>). Similar to the trend observed in Ni, the open-circuit potential ( $E_{\text{OCP}}$ ) was shifted in the negative direction under argon, and in the positive direction under both oxidizing atmospheres (Figure 4a). However,  $\beta$ -NiAl electrodes under both oxidizing atmospheres exhibited a frequent but aperiodic drop in open-circuit potential, followed by gradual recovery towards steady-state values. A sudden drop and gradual recovery of open-circuit potential clearly indicates an instability of the oxide scale in the electrolyte under oxidizing atmospheres, possibly in the form of localized damage (or transient pitting) in the oxide scale followed by repassivation [26]. Interestingly, the recovery time

was about 10–20 min under pure O<sub>2</sub>, but was longer (20–180 min) under O<sub>2</sub>-0.1%SO<sub>2</sub>, implying a more sluggish recovery (or passivation) of the oxide scale in O<sub>2</sub>-0.1%SO<sub>2</sub>.

**[Figure 4]**

The subsequent polarization measurements of the  $\beta$ -NiAl alloy clearly differentiated the electrochemical corrosion behavior in each gaseous atmosphere (Figure 4b). Compared to the lowest anodic currents in inert argon, the anodic currents increased by about three times under pure O<sub>2</sub>, and increased further by more than an order of magnitude under O<sub>2</sub>-0.1%SO<sub>2</sub>. Interestingly, the anodic currents under pure O<sub>2</sub> increased rapidly at large overpotentials above 0.40 V, suggesting a transpassive dissolution of the oxide scale. In general, the anodic currents of  $\beta$ -NiAl electrode were lower than those of Ni, indicating a decreased corrosion rate and better stability of the oxide scale on  $\beta$ -NiAl. However, the stability of the oxide scale in the electrolyte was questionable, in particular under oxidizing atmospheres due to the instability in open-circuit potentials, transpassive dissolution at large overpotentials (pure O<sub>2</sub>), and high anodic currents (O<sub>2</sub>-0.1%SO<sub>2</sub>).

Under both inert argon and oxidizing atmospheres, the formation of an alumina-rich oxide scale was confirmed by SEM-EDS and XRD (Figure 5). The alumina-rich scale thickness after a 12 h immersion test at 700 °C was measured to be ~8  $\mu$ m under argon, ~12  $\mu$ m under pure O<sub>2</sub>, and ~26  $\mu$ m under O<sub>2</sub>-0.1%SO<sub>2</sub>. The scale thickness in this work (> 8  $\mu$ m, 700 °C after 12 h) was much thicker compared to the results from gaseous oxidation studies [27–31] (e.g., ~8  $\mu$ m from  $\beta$ -NiAl, 1150 °C after 100 h in air [31] ) and other hot corrosion studies (e.g., < 1  $\mu$ m from Ni-36%Al coated with Na<sub>2</sub>SO<sub>4</sub>, 700 °C after 20 h in air [16] ). Such rapid scale growth is thought to come from the large volume of the electrolyte that allows continuous dissolution of oxide constituents (Al<sub>2</sub>O<sub>3</sub> and NiO). As shown in Figure 5a, both Ni and Al were detected in the salt layer even under

argon atmosphere, suggesting the dissolution of both NiO and Al<sub>2</sub>O<sub>3</sub>. In this regard, the rapid scale growth in this work involves the continuous dissolution of the oxide constituents from the scale and thus, is distinct from the compact oxide scale grown from gaseous oxidation controlled by solid-state diffusion. The formation of alumina-rich scale resulted in the Al-depleted region beneath the scale (brighter than the  $\beta$ -NiAl substrate in Figure 5a and Figure 5c) where internal oxidation was noticeable (dark color in the Al-depleted region). In this subscale region, the presence of  $\gamma'$ -Ni<sub>3</sub>Al was evident based on the XRD analysis (Figure 5d) and the composition of Al (30–38 mol%) where  $\gamma'$ -Ni<sub>3</sub>Al is stable. The co-existence of  $\beta$ -NiAl,  $\gamma'$ -Ni<sub>3</sub>Al, and Ni<sub>5</sub>Al<sub>3</sub> is probable at 700 °C and was reported in the literature after oxidation of Ni-36%Al (dry air, 700 °C after 20 h [16]); however, the definite phase constituents in the Al-depleted region were not clearly resolvable other than the  $\gamma'$ -Ni<sub>3</sub>Al phase by XRD and internal oxidation by SEM.

### [Figure 5]

Notably, the alumina-rich scale grown under O<sub>2</sub>-0.1%SO<sub>2</sub> was comprised of an adherent inner layer and a defective outer layer with micro-cracks (Figure 5c). The sulfur content (mol% S) was high at ~5% in the defective outer layer, compared to ~0.04% in the inner layer, suggesting the possibility to form aluminum sulfates (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>,  $T_m = 770$  °C) by reacting with SO<sub>3</sub> molecules:



Then, the formation of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> would provide an additional acidic dissolution pathway in O<sub>2</sub>-0.1%SO<sub>2</sub>:



, which aggravates the stability of oxide scale in O<sub>2</sub>-0.1%SO<sub>2</sub> and may contribute to the formation of micro-cracks which were not observed in Ar and pure O<sub>2</sub>. While the exact nature of micro-crack formation is not fully understood and will require further investigation, the highest anodic currents

in O<sub>2</sub>-0.1%SO<sub>2</sub> (Figure 4b) could be attributed to the aggravated stability of oxide scale resulting from the formation/dissolution of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and micro-cracks.

Compared to Ni under pure O<sub>2</sub>, the alumina-rich scale from  $\beta$ -NiAl served as a barrier layer against severe degradation reactions of Ni/NiO in the sulfate-containing electrolyte and improved corrosion resistance; however, the instability of alumina-rich scale was evident from electrochemical corrosion behavior and characterization of corrosion scale. Moreover, the stability of alumina-rich scale was severely deteriorated in O<sub>2</sub>-0.1%SO<sub>2</sub>, leading to high anodic currents comparable to those of pure Ni.

### **3.3 Electrochemical behavior and the corrosion scale of $\beta$ -NiAl/Cr alloy**

The addition of 5 mol% Cr into  $\beta$ -NiAl ( $\beta$ -NiAl/Cr, 47.5-47.5-5 mol%) resulted in a much less frequent drop in open-circuit potential compared to  $\beta$ -NiAl, indicating enhanced stability of the oxide layer in both oxidizing atmospheres of pure O<sub>2</sub> and O<sub>2</sub>-0.1%SO<sub>2</sub> (Figure 6a). In contrast to  $\beta$ -NiAl which exhibited increased anodic currents from pure O<sub>2</sub> to O<sub>2</sub>-0.1%SO<sub>2</sub> by an order of magnitude (Figure 4b), the  $\beta$ -NiAl/Cr alloys could maintain low anodic currents under both oxidizing atmospheres (Figure 6b), indicating the beneficial effect of Cr against hot corrosion, especially under O<sub>2</sub>-0.1%SO<sub>2</sub>.

#### **[Figure 6]**

The cross-section analyses of the corrosion layer from the  $\beta$ -NiAl/Cr sample in each oxidizing atmosphere are displayed in Figure 7. Under both atmospheres of pure O<sub>2</sub> and O<sub>2</sub>-0.1%SO<sub>2</sub>, the thickness of external scale was ~8  $\mu$ m for  $\beta$ -NiAl/Cr, compared to 12–26  $\mu$ m for  $\beta$ -NiAl, and internal oxidation was also observed in the substrate. Interestingly, the external scale was comprised of both Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub>; however, Cr<sub>2</sub>O<sub>3</sub> was enriched in the outer layer and depleted in the inner layer. The composition of Cr by EDS was about 9–14 mol% in the outer layer,

but was less than 0.8 mol% in the inner layer. While the diffraction peaks from  $\text{Al}_2\text{O}_3$  were identified by XRD (Figure 7c), the crystalline  $\text{Cr}_2\text{O}_3$  phase was not evident in the oxide scale, possibly due to the formation of a solid solution ( $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ ).

### [Figure 7]

The beneficial effects of Cr into  $\beta\text{-NiAl}$  under oxidizing atmospheres are well supported by a more stable open-circuit potential response, lower anodic currents (Figure 6), and thinner oxide scales on  $\beta\text{-NiAl/Cr}$  than  $\beta\text{-NiAl}$  (Figure 7), which could be associated with the mixed-oxide ( $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ ) scale acting as a corrosion barrier. In hot corrosion processes, the beneficial effects of Cr were postulated to occur due to the minimal solubility of  $\text{Cr}_2\text{O}_3$  under typical oxidizing atmospheres found in gas turbines ( $\text{O}_2\text{-SO}_2\text{-SO}_3$ ) as well as the positive gradient of oxide solubility in the salt film (fluxing mechanisms) [12,13]. In this regard, the enrichment of  $\text{Cr}_2\text{O}_3$  at the scale-electrolyte interface could be attributed to a more rapid dissolution of  $\text{Al}_2\text{O}_3$  than  $\text{Cr}_2\text{O}_3$  from the mixed-oxide ( $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ ) scale, resulting in unique morphology distinct from the compact scale morphologies from gaseous oxidation controlled by solid-state diffusion in ternary Ni-Cr-Al alloys (e.g., dual layers of  $\text{Cr}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  in air at 1200 °C) [32]. The formation of a mixed oxide ( $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ ) scale resulted in the depletion of both Al and Cr in the subscale region where the approximate composition (mol%) of Al by EDS was ~41% in pure  $\text{O}_2$ , ~29% in  $\text{O}_2\text{-0.1\%SO}_2$ , and the Cr content was slightly less than 1% Cr. The presence of  $\gamma'\text{-Ni}_3\text{Al}$  phase confirmed by XRD (Figure 7c) and the depletion of both Al and Cr by SEM, suggest that the phase constituents in the Al/Cr-depleted region may resemble those from  $\beta\text{-NiAl}$  (discussed in section 3.2) but are inconclusive beyond the  $\gamma'\text{-Ni}_3\text{Al}$  phase and internal oxidation.

### 3.4. Effects of Al and Cr in hot corrosion resistance of Ni alloys

In each gaseous atmosphere, polarization curves of three Ni alloys were compared and further analyzed to contrast the effects of Al and Cr addition (Figure 8). Based on the stable anodic currents observed at an overpotential range of 0.10–0.30 V ( $\log |j|$  vs.  $\eta$ ) in each curve, corrosion current density ( $j_{\text{corr}}$ ) was evaluated by extrapolation into corrosion potential ( $E_{\text{corr}}$ ), similar to an approach used for Tafel extrapolation under active dissolution of corroding metal [33,34]. Unlike typical passivation characteristics in an aqueous system near room temperature, the anodic currents continued to increase in sulfate-containing molten salts at 700 °C. The analyzed results are summarized in Table 1, including the estimated anodic slope ( $d \log j / d\eta$ ) as well as the corrosion scale thickness obtained from immersion tests by SEM.

**[Figure 8]**

**[Table 1]**

In inert argon, comparable corrosion current densities (0.25–0.26 mA/cm<sup>2</sup>) were obtained for both Ni and  $\beta$ -NiAl electrodes; however, the lower slope ( $d \log j / d\eta$ ) for  $\beta$ -NiAl than Ni indicates a better stability of alumina-rich scale than NiO scale during anodic polarization (Figure 8a). In pure O<sub>2</sub>, the corrosion current density of Ni substantially increased to 11.97 mA/cm<sup>2</sup>, compared to 0.78 mA/cm<sup>2</sup> for  $\beta$ -NiAl and 0.55 mA/cm<sup>2</sup> for  $\beta$ -NiAl/Cr alloys, indicating enhanced hot corrosion resistance of alumina-rich or mixed-oxide (Al<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>) scales (Figure 8b). However, the addition of 0.1%SO<sub>2</sub> resulted in an increased corrosion current density of  $\beta$ -NiAl at 8.86 mA/cm<sup>2</sup> (Figure 8c), compared to 0.78 mA/cm<sup>2</sup> in pure O<sub>2</sub>, due to the defective oxide scale (Figure 5c). In contrast, the corrosion current densities of  $\beta$ -NiAl/Cr were the lowest among the tested Ni alloys at 0.09 mA/cm<sup>2</sup> in O<sub>2</sub>-0.1%SO<sub>2</sub> and 0.55 mA/cm<sup>2</sup> in pure O<sub>2</sub>. In other words, hot corrosion performance of  $\beta$ -NiAl/Cr alloys was enhanced by forming an external scale that incorporates both Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> under oxidizing atmospheres.

#### 4. CONCLUSIONS

Electrochemical corrosion properties of Ni alloys (Ni,  $\beta$ -NiAl, and  $\beta$ -NiAl/Cr) were determined in molten LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> electrolyte under three different gaseous atmospheres (inert argon, pure O<sub>2</sub>, and O<sub>2</sub>-0.1%SO<sub>2</sub>) at 700 °C. Pure Ni developed a uniform NiO layer only in the inert argon atmosphere, and rapidly degraded in oxidizing atmospheres due to the instability of NiO which resulted in a thick corrosion scale comprised of NiO dispersed in the salt, nickel sulfides, and nickel sulfate. The  $\beta$ -NiAl alloys developed alumina-rich scales under oxidizing atmospheres with an indication of local breakdown of the oxide scale during open-circuit potential measurements. Moreover, the  $\beta$ -NiAl alloy performed poorly in O<sub>2</sub>-0.1%SO<sub>2</sub>, indicated by a high corrosion current density and defective oxide scale with micro-cracks. The addition of 5 mol% Cr in  $\beta$ -NiAl ( $\beta$ -NiAl/Cr alloy) enhanced corrosion resistance both under pure O<sub>2</sub> and O<sub>2</sub>-0.1%SO<sub>2</sub>, indicated by the lowest corrosion current density among the tested alloys and the formation of external oxide scales comprised of both Cr<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>. Overall, hot corrosion resistance of Ni alloys in the sulfate-containing molten salt was affected by gaseous atmosphere and alloying elements (Al and Cr), both of which controlled the formation of oxide scales as well as their stability in corrosive molten salt solution.

#### Author Contribution

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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### **Data Availability**

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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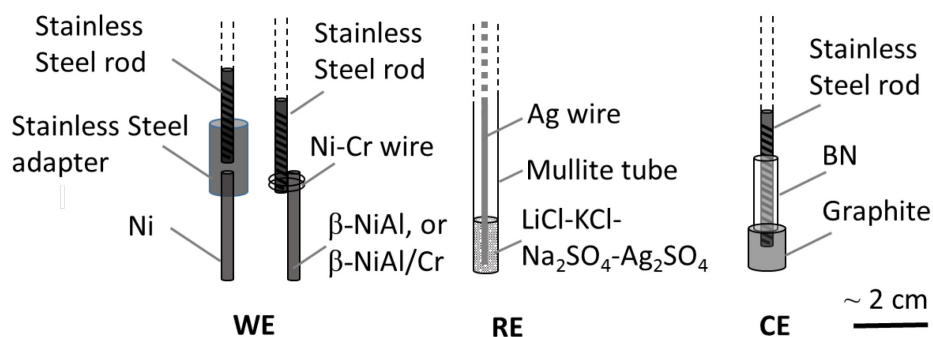
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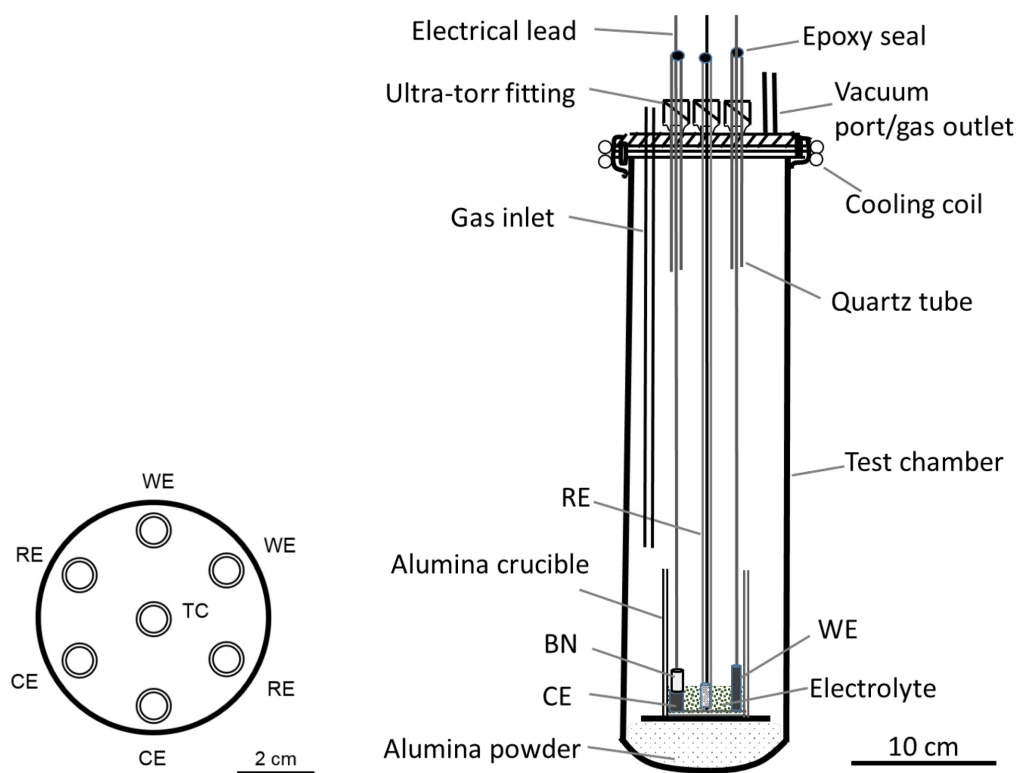
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## FIGURES AND TABLES

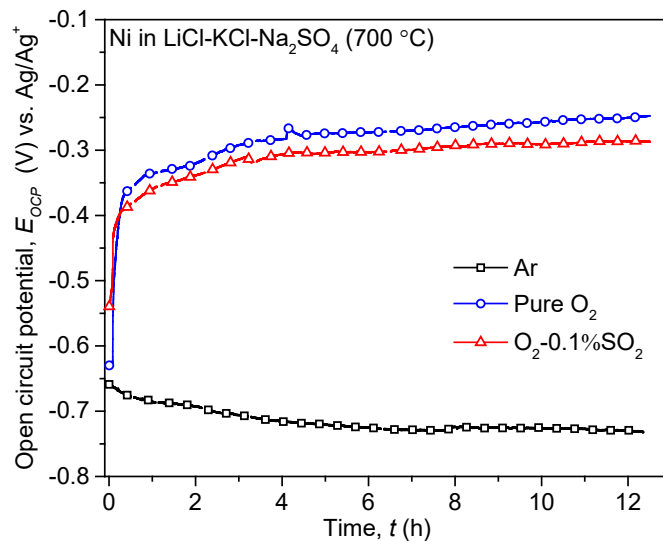


**Figure 1a.**

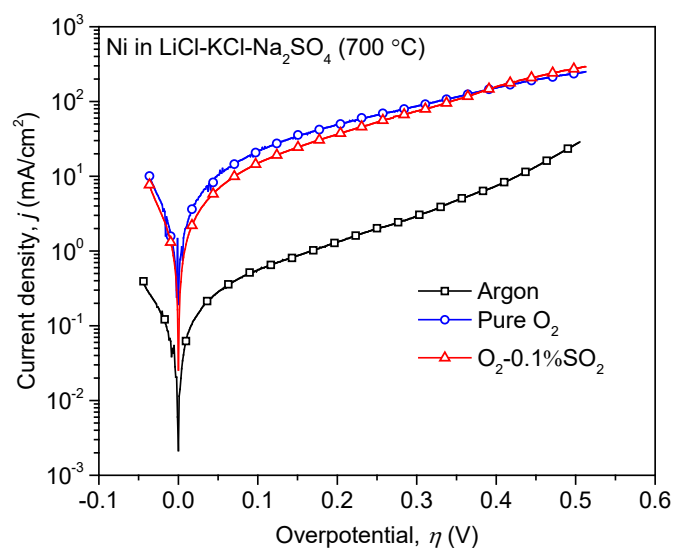


**Figure 1b.**

**Figure 1.** Schematic of three-electrode electrochemical cell: (a) approximate electrode geometry for working (WE), reference (RE), and counter (CE) electrodes, and (b) top view of electrode configuration (left) in a test chamber assembly (right).



**Figure 2a.**



**Figure 2b.**

**Figure 2.** Electrochemical behavior of pure Ni in molten LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> (53.3-36.7-10 mol%) solution at 700 °C in three different gaseous atmospheres of argon, pure O<sub>2</sub>, and O<sub>2</sub>-0.1%SO<sub>2</sub>. (a) Open-circuit potential measurements for 12 h and (b) potentiodynamic polarization curve (log | $j$ | vs.  $\eta$ ) at a scan rate of 1 mV/s over  $-0.05 \text{ V} < \eta < 0.50 \text{ V}$ .

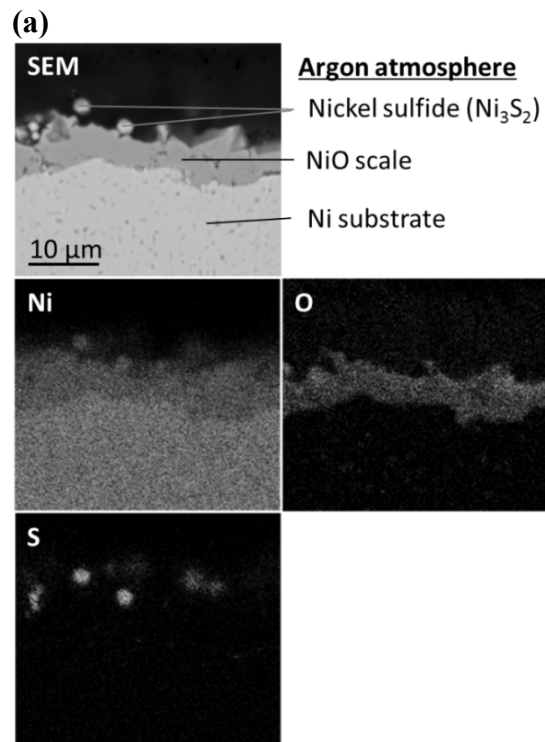


Figure 3a.

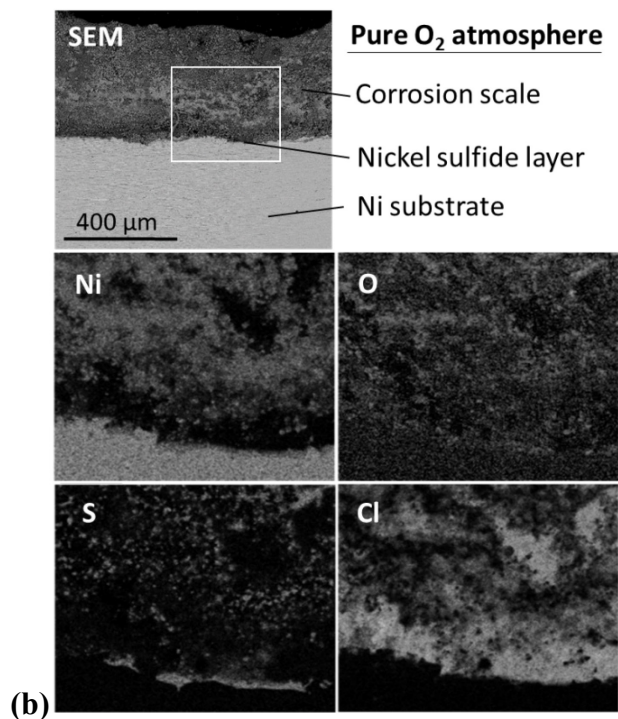


Figure 3b.

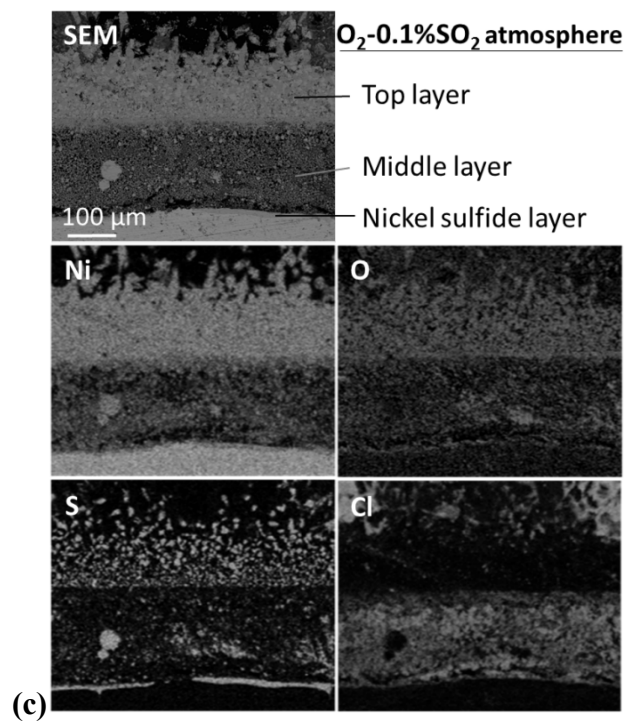
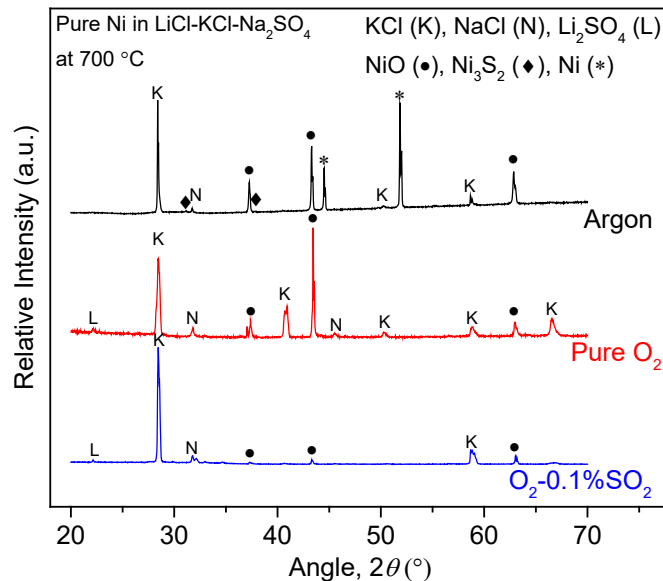
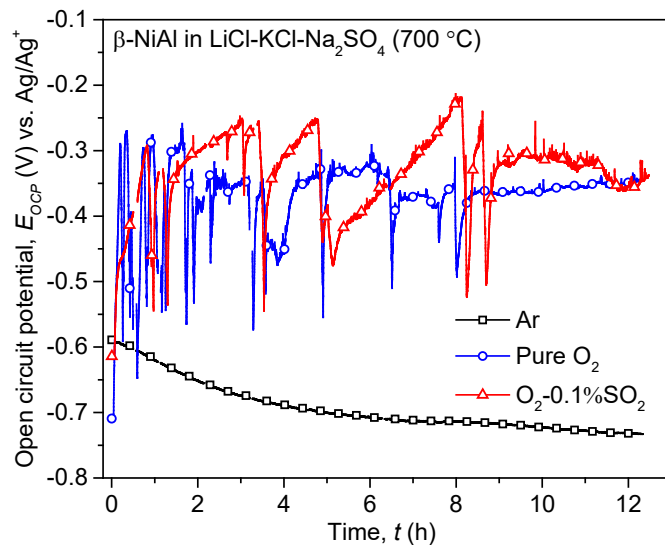


Figure 3c.

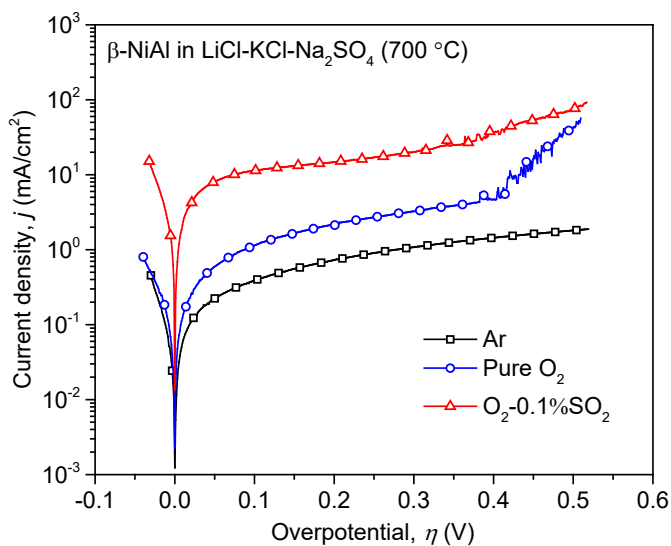


**Figure 3d.**

**Figure 3.** (a-c) Back-scattered SEM and elemental X-ray mapping images of pure Ni samples after immersion tests for 12 h in molten  $LiCl-KCl-Na_2SO_4$  (53.3-36.7-10 mol%) solution at 700  $^{\circ}C$  in each gaseous atmosphere of (a) argon, (b) pure  $O_2$ , and (c)  $O_2$ -0.1% $SO_2$ . (d) XRD patterns from the corroded Ni surface.

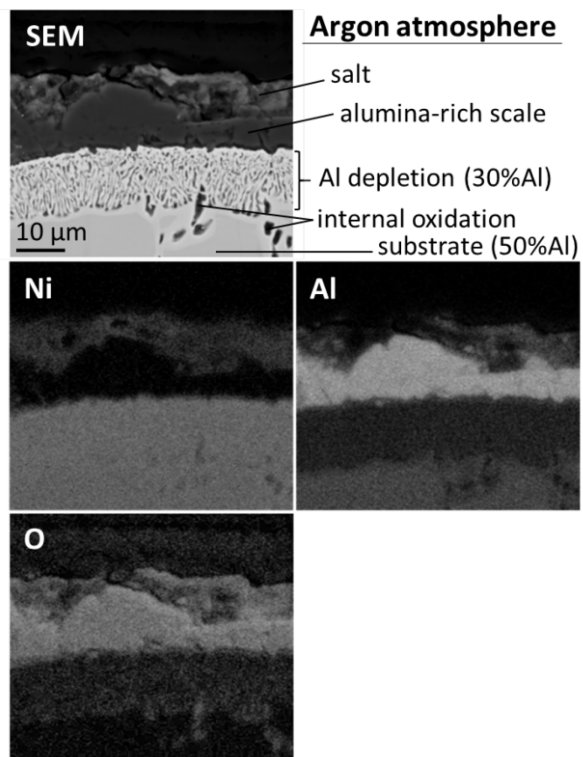


**Figure 4a.**

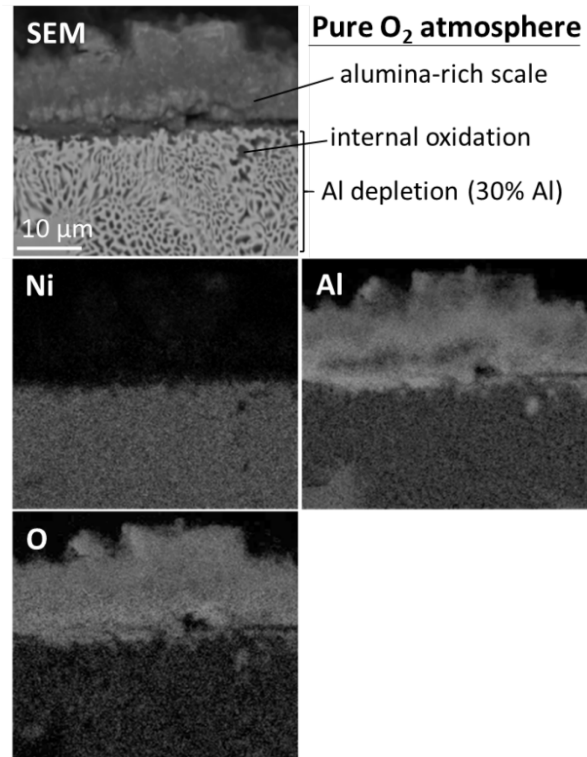


**Figure 4b.**

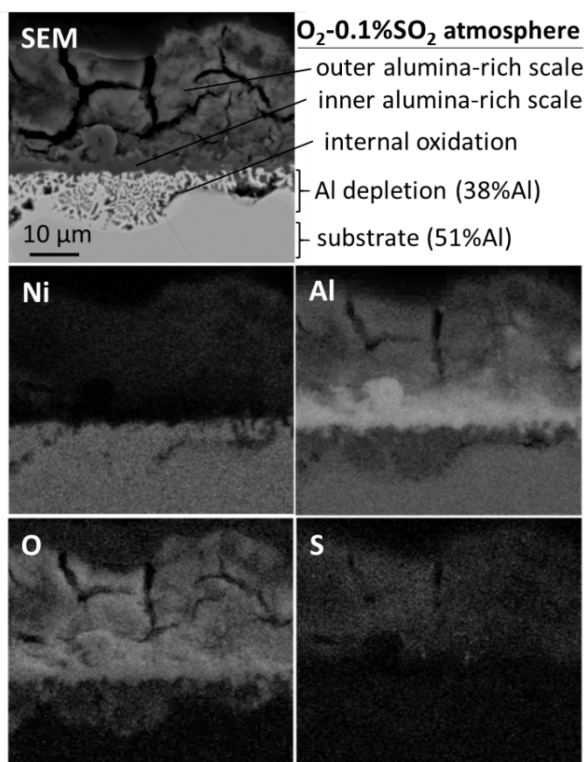
**Figure 4.** Electrochemical behavior of  $\beta$ -NiAl alloys in molten LiCl-KCl- $\text{Na}_2\text{SO}_4$  (53.3-36.7-10 mol%) solution at 700 °C in three different gaseous atmospheres of argon, pure  $\text{O}_2$ , and  $\text{O}_2$ -0.1% $\text{SO}_2$ . (a) Open-circuit potential measurements for 12 h and (b) potentiodynamic polarization curve ( $\log |j|$  vs.  $\eta$ ) at a scan rate of 1 mV/s over  $-0.05 \text{ V} < \eta < 0.50 \text{ V}$ .



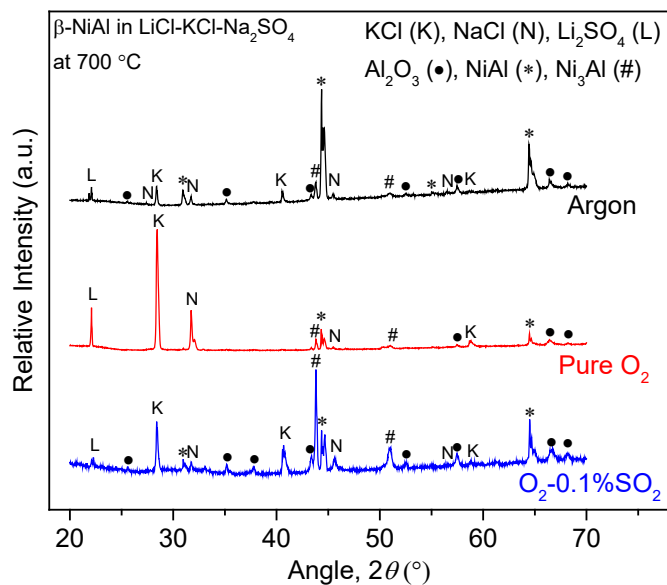
**Figure 5a.**



**Figure 5b.**

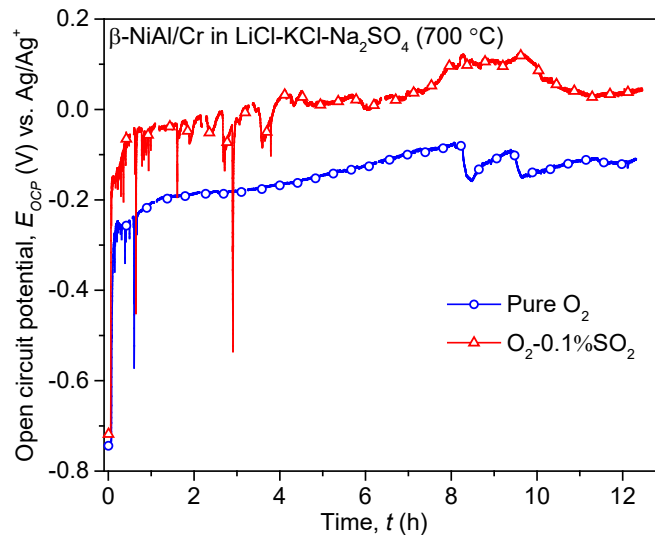


**Figure 5c.**

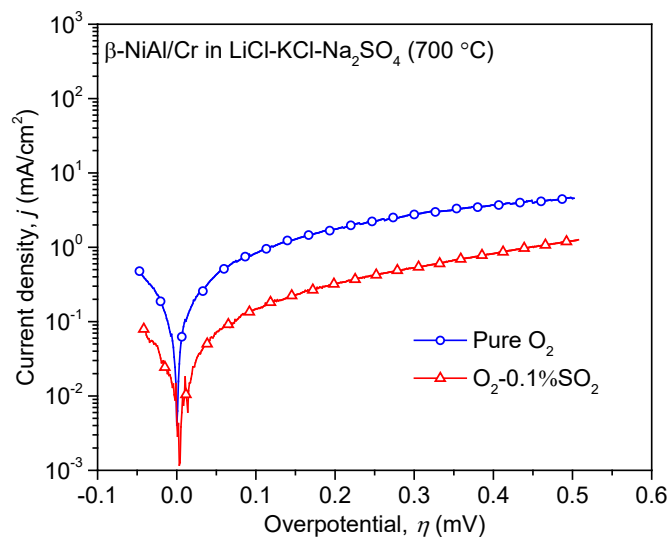


**Figure 5d.**

**Figure 5.** (a-c) Back-scattered SEM and elemental X-ray mapping images of  $\beta$ -NiAl alloys after immersion tests for 12 h in molten  $LiCl$ - $KCl$ - $Na_2SO_4$  (53.3-36.7-10 mol%) solution at 700  $^{\circ}C$  in each gaseous atmosphere of (a) argon, (b) pure  $O_2$ , and (c)  $O_2$ -0.1% $SO_2$ . (d) XRD patterns from the corroded  $\beta$ -NiAl surface.

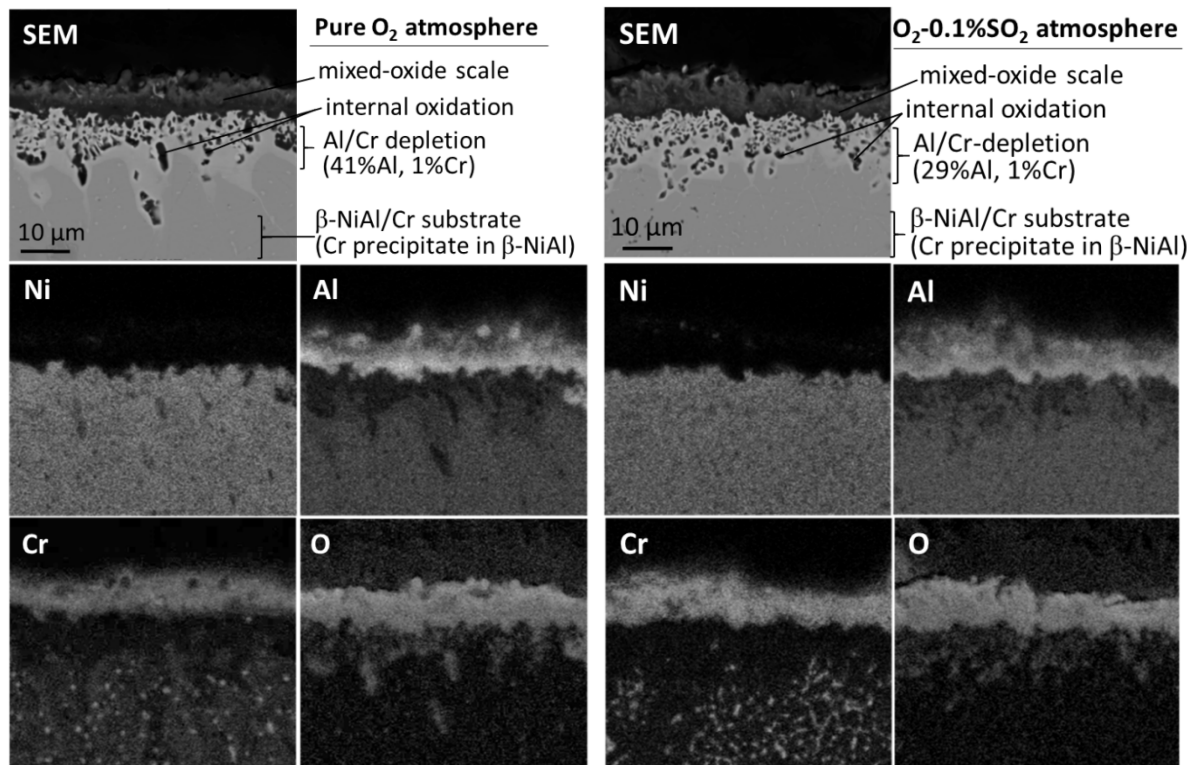


**Figure 6a.**



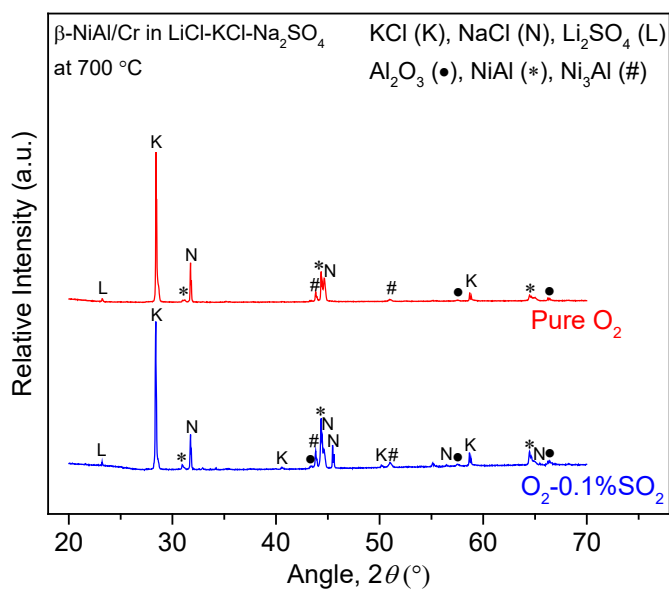
**Figure 6b.**

**Figure 6.** Electrochemical behavior of  $\beta$ -NiAl/Cr (47.5-47.5-5 mol%) alloys in molten LiCl-KCl- $\text{Na}_2\text{SO}_4$  (53.3-36.7-10 mol%) solution at 700 °C in oxidizing atmospheres of pure  $\text{O}_2$ , and  $\text{O}_2$ -0.1% $\text{SO}_2$ . (a) Open-circuit potential measurements for 12 h and (b) potentiodynamic polarization curve ( $\log |j|$  vs.  $\eta$ ) at a scan rate of 1 mV/s over  $-0.05 \text{ V} < \eta < 0.50 \text{ V}$ .



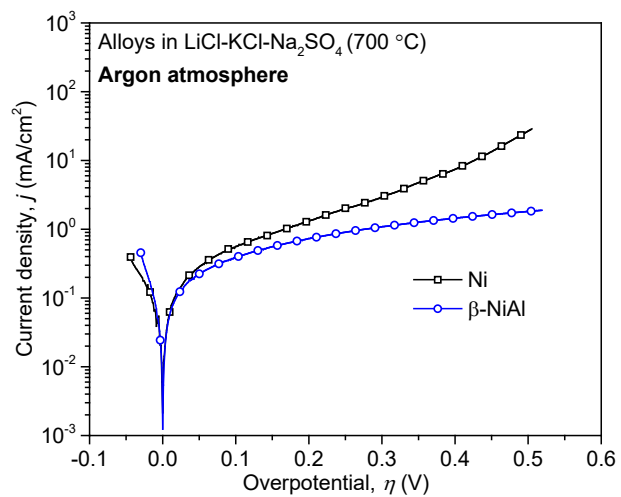
**Figure 7a.**

**Figure 7b.**

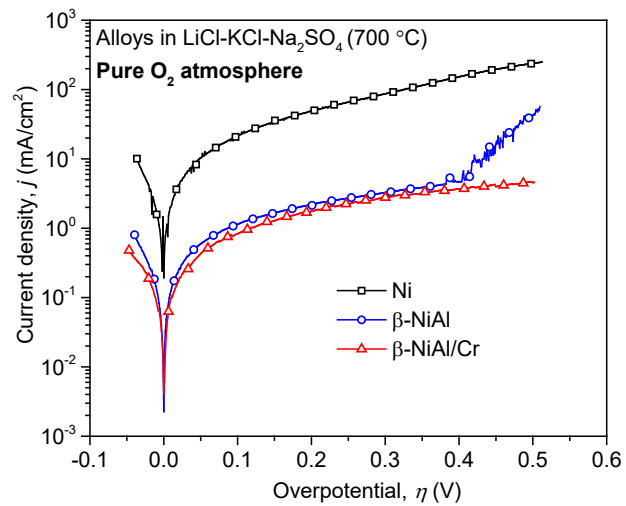


**Figure 7c.**

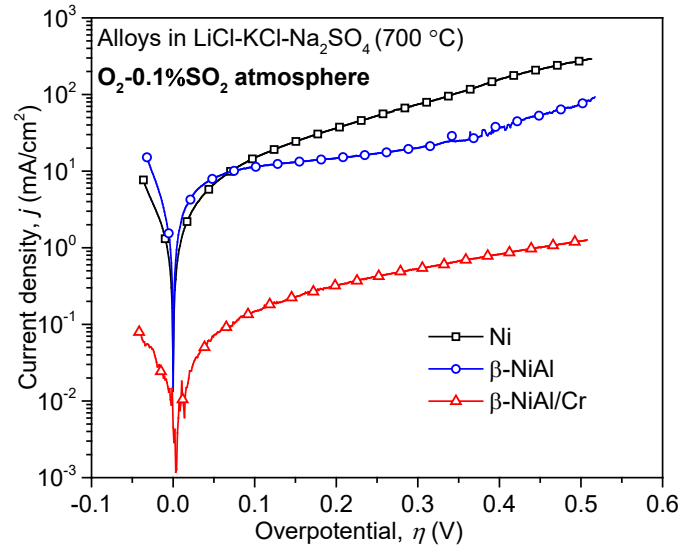
**Figure 7.** (a-b) Back-scattered SEM and elemental X-ray mapping images of β-NiAl/Cr (47.5-47.5-5 mol%) alloys after immersion tests for 12 h in molten LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> (53.3-36.7-10 mol%) solution at 700 °C in each gaseous atmosphere of (a) pure O<sub>2</sub> and (b) O<sub>2</sub>-0.1%SO<sub>2</sub>. (c) XRD patterns from the corroded β-NiAl/Cr surface.



**Figure 8a.**



**Figure 8b.**



**Figure 8c.**

**Figure 8.** Potentiodynamic polarization curves ( $\log |j|$  vs.  $\eta$ ) of Ni alloys in (a) argon, (b) pure O<sub>2</sub>, and (c) O<sub>2</sub>-0.1%SO<sub>2</sub>, at a scan rate of 1 mV/s at 700 °C after 12 h immersion in LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> electrolyte.

**Table 1.** Corrosion potential ( $E_{\text{corr}}$ ), corrosion current density ( $j_{\text{corr}}$ ), and the slope ( $d \log j / d\eta$ ), estimated from polarization curve of Ni alloys over  $0.10 \text{ V} < \eta < 0.30 \text{ V}$  in each gaseous atmosphere, as well as corrosion scale thickness. Measured after immersion for 12 h at  $700^\circ\text{C}$  in LiCl-KCl- $\text{Na}_2\text{SO}_4$  (53.3-36.7-10 mol%) electrolyte.

| Gaseous atmosphere               | Alloy            | $E_{\text{corr}}$ vs. $\text{Ag}/\text{Ag}^+$ (V) | $j_{\text{corr}}$ ( $\text{mA}/\text{cm}^2$ ) | $d \log j / d\eta$ (dec/V) | Scale thickness ( $\mu\text{m}$ ) |
|----------------------------------|------------------|---------------------------------------------------|-----------------------------------------------|----------------------------|-----------------------------------|
| Ar                               | Ni               | -0.75                                             | 0.26                                          | 3.56 ( $\pm 0.01$ )        | 5.0 ( $\pm 1.5$ )                 |
|                                  | $\beta$ -NiAl    | -0.76                                             | 0.25                                          | 2.16 ( $\pm 0.02$ )        | 8 ( $\pm 3$ )                     |
| $\text{O}_2$                     | Ni               | -0.25                                             | 11.97                                         | 2.90 ( $\pm 0.02$ )        | 374 ( $\pm 20$ )                  |
|                                  | $\beta$ -NiAl    | -0.20                                             | 0.78                                          | 2.18 ( $\pm 0.02$ )        | 12 ( $\pm 2$ )                    |
|                                  | $\beta$ -NiAl/Cr | -0.10                                             | 0.55                                          | 2.47 ( $\pm 0.03$ )        | 8 ( $\pm 1.2$ )                   |
| $\text{O}_2$ -0.1% $\text{SO}_2$ | Ni               | -0.30                                             | 7.03                                          | 3.42 ( $\pm 0.01$ )        | 143 ( $\pm 12$ )                  |
|                                  | $\beta$ -NiAl    | -0.40                                             | 8.86                                          | 1.19 ( $\pm 0.01$ )        | 26 ( $\pm 3$ )                    |
|                                  | $\beta$ -NiAl/Cr | +0.05                                             | 0.09                                          | 2.71 ( $\pm 0.02$ )        | 7.5 ( $\pm 1.5$ )                 |