

# Monitoring the Degradation Process of Inconel 600 and its Aluminide Coatings under Molten Sulfate Film with Thermal Cycles by Electrochemical Measurements

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With a specially designed electrochemical cell, the changes in impedance behavior for Inconel 600 and aluminide diffusion coatings under molten sulfate film with thermal cycles (from 800 °C to 350 °C) were monitored with electrochemical impedance measurements. It was found that corrosion resistance for both materials increased with lower temperatures. At the same time, the state of molten salt was also monitored successfully by measuring the changes in impedance at high frequency, which generally represents the resistance of molten salt itself. After two thermal cycles, both Inconel 600 and aluminide diffusion coatings showed excellent corrosion resistance. The results from SEM observation and EDS analysis correlated well with the results obtained by electrochemical impedance measurements. It is concluded that electrochemical impedance is very useful for monitoring the corrosion resistance of materials under molten salt film conditions even with thermal cycles.

**Keywords :** hot corrosion, molten salt film, thermal cycle, EIS, aluminide diffusion coating, Inconel 600

## 1. Introduction

Hot corrosion occurs on the metallic components in gas turbine or boilers<sup>1)</sup>. Recently, furnaces used for burning waste also encounter hot corrosion since the operating temperature has been raised greatly in order to achieve higher burning efficiency. Different from high temperature oxidation which is a dry degradation process, hot corrosion happens with the existence of molten salt film on the surface of metallic components. The thin molten salt film is formed by the reactions between impurities from fuel and substances from the environment such as sodium chloride. It can cause accelerated corrosion and give catastrophic damage to metallic components of those industrial equipment or devices. Since the molten salts are electrolytes, electrochemical methods are considered to be very useful for understanding the corrosion mechanism and monitoring the changes in corrosion resistance of alloys and protective coatings. Many researchers have done a lot work on hot corrosion with electrochemical methods but most of the experiments were conducted under bulk molten salt condition<sup>2-4)</sup>. However, molten salt exists as

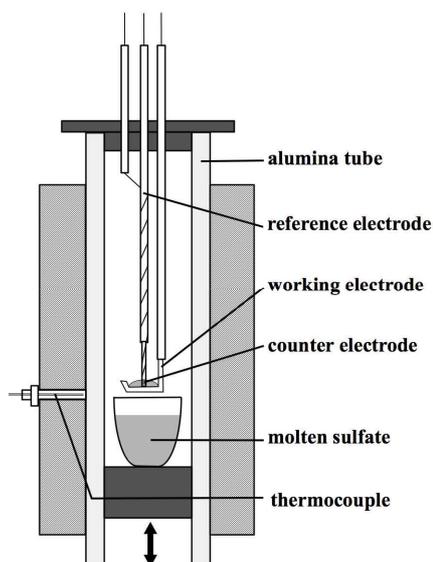
a thin film on metallic materials under practical industrial environment. One big difference between bulk molten salt and thin molten salt film is the effect of oxygen and other gases on the degradation process of materials. Since the diffusion of environmental gases is much faster under molten salt film than in the bulk molten salt, the corrosion resistance or the corrosion mechanism may vary. Therefore, it is doubtful that it is the right way to evaluate hot corrosion resistance of alloys and protective coatings with electrochemical methods in bulk molten salt. Even if some researchers have been conducted their experiments under a conditions similar to molten salt film, it is still not very clear that whether the results obtained in bulk molten salt can perfectly explain or give the right information about the practical hot corrosion that happens with the existence of molten salt film.

The corrosion of alloys and coatings under molten salt film condition has been carried out in our lab with electrochemical techniques, such as measuring changes in corrosion potential, Tafel extrapolation from polarization curves and electrochemical impedance spectroscopy (EIS)<sup>5-8)</sup>. In our previous researches, corrosion behavior and corrosion rates of alloys were investigated by potentiodynamic polarization under molten sulfate film condition. It was con-

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**Table 1. Chemical composition of Inconel 600**

Fe	Ni	Cr	Mn	C
6-10	>72	15.7	<0.1	<0.15

**Fig. 1.** Electrochemical cell designed for electrochemical measurements under molten salt film condition.

cluded that under molten sulfate film condition, the oxygen partial pressure had significant effect on polarization behavior of alloys. Corrosion rates of alloys changed greatly with the change of atmosphere (change in oxygen partial pressure). We also applied EIS techniques to monitor the changes in impedance behaviors and corrosion resistance of alloys and protective coatings under molten salt film condition with an electrochemical cell designed especially for electrochemical measurements under molten salt condition<sup>8</sup>). In this study, in order to simulate the operating conditions for alloys and protective coatings more practically, the degradation processes of Inconel 600 and aluminide diffusion coatings were monitored by electrochemical impedance measurements under molten sulfate film with thermal cycles.

## 2. Experimental Procedure

Inconel 600 alloy and its aluminide diffusion coatings were used in this study. The chemical composition of Inconel 600 is shown in Table 1. Aluminide diffusion coatings on Inconel 600 were prepared by pack cementation method. As the substrate for aluminide diffusion coatings, Inconel 600 sample was polished by sanding paper to 2000 grit. After being cleaned in ultrasonic bath with acetone, it was put into a mixture powder of Al, Al<sub>2</sub>O<sub>3</sub>

and NH<sub>4</sub>Cl (Al<sub>2</sub>O<sub>3</sub> 75 wt%, Al 20 wt%, NH<sub>4</sub>Cl 5 wt%) and then treated at 800 °C for 2 hours under argon atmosphere.

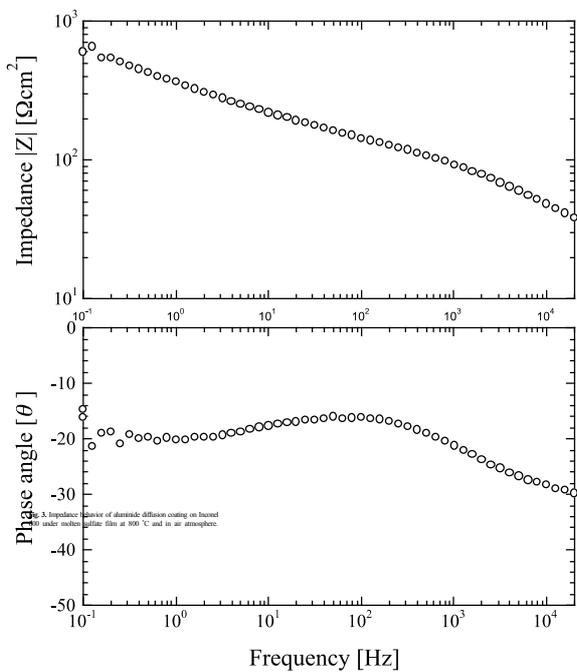
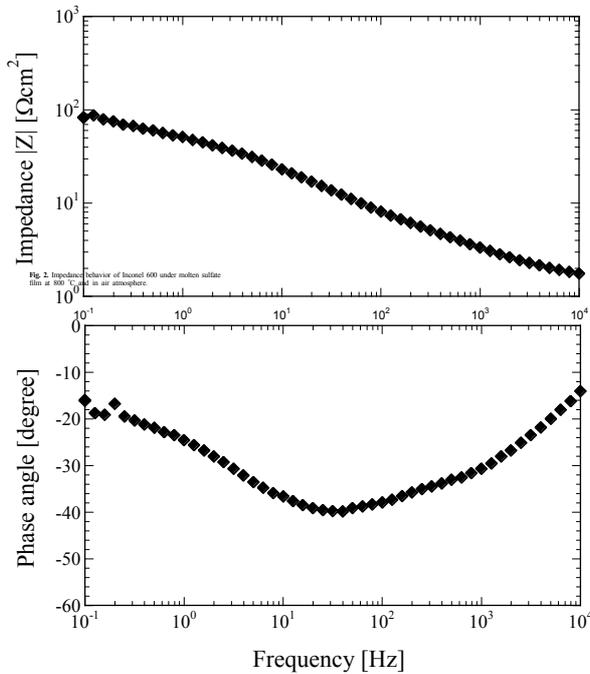
A mixture of 50 mol% Na<sub>2</sub>SO<sub>4</sub> - 50 mol% Li<sub>2</sub>SO<sub>4</sub> was used as the resource of molten salt film. The melting point of the mixture was confirmed as 470 °C by differential thermal analysis (DTA). In order to monitor the behavior of both alloys and molten salt film itself, temperature range for thermal cycle was set from 350 °C to 800 °C and two cycles were applied during the electrochemical impedance measurements. A special electrochemical cell was designed for electrochemical impedance measurements under molten salts film. Fig.1 shows the schematic diagram of the special designed electrochemical cell. In order to fit the specially designed electrochemical cell, each sample (3 mm in width and 100 mm in length) was fabricated into an "L" shape. Reference electrode, which is Ag/Ag<sup>-1</sup> electrode sealed in a mullite tube, was set on the surface of working electrode and the counter electrode, the platinum wire was wrapped on the reference electrode. Right before the start of electrochemical measurements, the crucible filled with molten sulfate was lifted up to let the electrodes to be immersed into molten sulfate for few seconds. Then the crucible was lower down and a molten salt film was left on the electrodes.

The monitoring of hot corrosion process of alloys and aluminide diffusion coatings was conducted by electrochemical impedance technique with a three-electrode cell arrangement. A sinusoidal perturbation of 10 mV was applied to the system. The current response was measured over a range of frequency from 1 × 10<sup>4</sup> Hz to 10<sup>-1</sup> Hz. The corrosion rates of samples were monitored by continuous measurement of impedance at a low frequency (1 × 10<sup>-1</sup> Hz). Before or after electrochemical measurements, surface morphology and cross section profile for some samples were observed. Elements distribution in coating layer for aluminide diffusion coatings was examined by energy-dispersive X-ray spectroscopy (EDS).

## 3. Results and Discussion

### 3.1 Impedance behaviors of Inconel 600 and aluminide diffusion coatings

Fig. 2 shows the impedance behavior of Inconel 600 under molten sulphate film at 800 °C. In the case of Inconel 600, even if the thin molten sulfate film caused some distribution effect, the impedance showed one time constant behavior. It is considered that a simple equivalent circuit can represent the properties of the interface between Inconel 600 alloy and molten sulfate. Therefore, impedance at low frequency represents the corrosion re-



sistance  $R_c$  and the impedance at high frequency represents the molten film solution resistance  $R_s$ . In this case, by monitoring the impedance changes at different frequencies, information about the change of corrosion resistance, solution resistance or the change in molten salt film itself

can be obtained.

The impedance behavior of aluminate diffusion coating on Inconel 600 under molten salt film at 800 °C was shown in Fig. 3. Different from Fig. 2, there is a relatively large phase shift in high frequency area and the impedance at high frequency is also higher than that of Inconel 600. Our previous study confirmed that the impedance component shown at high frequency represents the characteristics of alumina formed on the surface of aluminate diffusion coating<sup>5,6</sup>. The phase shift at high frequency is due to the capacitive properties of the alumina scale and the higher impedance value compared to that for Inconel 600 alloy at high frequency area represents not only the solution resistance  $R_s$  but a total of  $R_s$  and the resistance of oxide film  $R_f$ <sup>7</sup>. On the other hand, as observed for the alloys, impedance at low frequency region represents the corrosion resistance  $R_c$ . Therefore, in the case of aluminate diffusion coating, information about the electrochemical reaction (corrosion resistance) and the alumina film can be obtained at the same time by monitoring the changes in impedance at different frequencies.

### 3.2. Monitoring the degradation processes under thermal cyclic condition

Fig. 4 shows the changes of corrosion resistance  $R_c$  and solution resistance  $R_s$  with thermal cycles for Inconel 600. Thermal cycle started from 800 °C. Corrosion resistance  $R_c$  kept on increasing gradually with the dropping of temperature. Meanwhile, In the case of solution resistance  $R_s$  for Inconel 600 shown in Fig. 4, the value of  $R_s$  also increased at a constant changing rate with the decrease at the temperature range from 800 °C to 470 °C. Then, the increasing of  $R_s$  became faster and when temperature dropped to 440 °C, solution resistance  $R_s$  increased abruptly to a high value and kept on increasing with the dropping of temperature and the value of  $R_s$  became almost the same as  $R_c$  at the peak point. Then, when temperature started to increase in one thermal cycle,  $R_s$  began to decrease greatly and became the same order of value finally as that before the abrupt increase. Same phenomenon appeared again during the second thermal cycle. As mentioned before, the melting point for the mixture of sulfates used in this study was confirmed to be 470 °C by DTA. Therefore, The abrupt increase of  $R_s$  is because the molten salt film changed from liquid state to solid state. The impedance measurement can not only monitor the change in corrosion resistance but also give information about the state of molten salt film.

The monitoring results for aluminate diffusion coating are shown in Fig. 5. Similar to the results for Inconel 600, corrosion resistance  $R_c$  increased with the decreasing

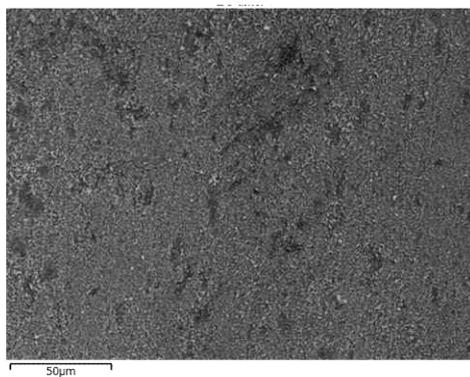
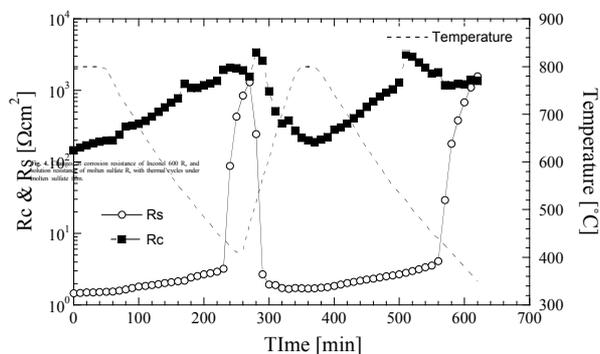


Fig. 6. Surface morphology for Inconel 600 after two thermal cycles test under molten sulfate film, air atmosphere.

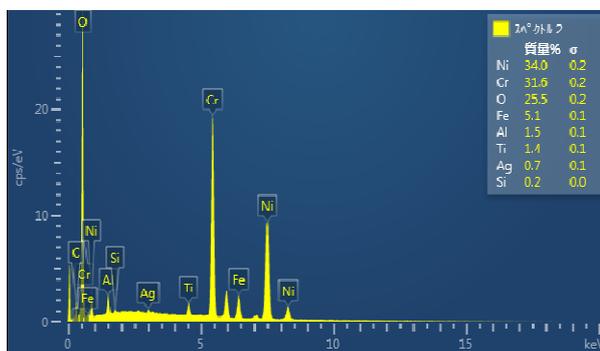
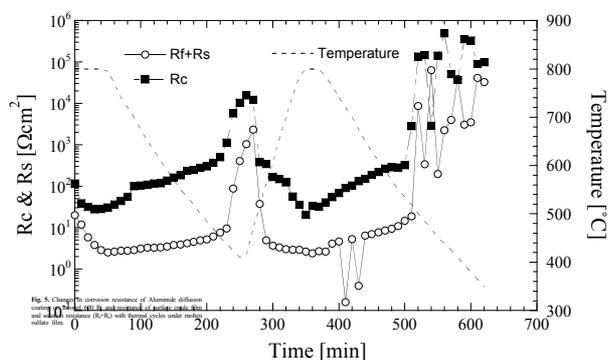


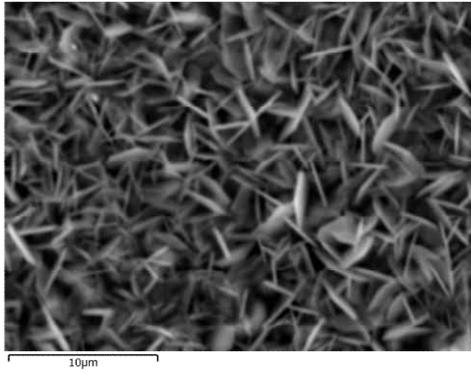
Fig. 7. Result of EDS analysis for Inconel 600 after two thermal cycles test under molten sulfate film, air atmosphere.

of temperature and decreased with the increasing of temperature during one thermal cycle. Since the impedance value at high frequency area represents total amount of resistance from aluminum oxide film  $R_f$  and solution resistance of molten salt  $R_s$ , mixed information was obtained from Fig. 5. During the temperature range from 800 °C to 470 °C, the relative higher value of resistance compared to that of Inconel 600 (Fig. 4) is due to the resistance of aluminum oxide film formed on coating surface. When temperature was lowered below the melting point of the molten salt, solution resistance increased greatly, meaning the salt film changed from liquid to solid. In the case of aluminide coating, there were some unstable results especially at the end of second thermal cycle. The reason for it is considered to be the roughness of the coating surface and the changes of coating layer with temperature. For both Inconel 600 and aluminide diffusion coating, the corrosion resistance in second thermal cycle recovered to almost the same value as in the first cycle, it is concluded from impedance monitoring that both Inconel 600 and aluminide diffusion coating remained their good corrosion

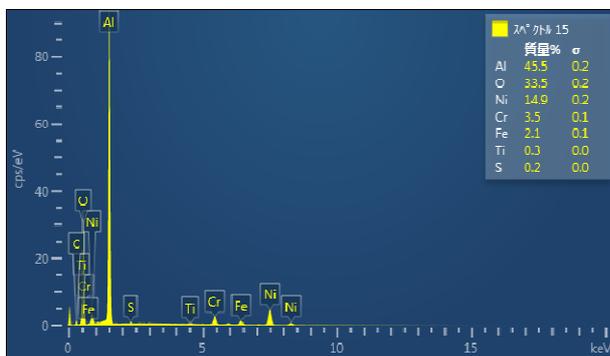
resistance after two thermal cycles.

### 3.3 Results of SEM observation and EDS analysis

In order to confirm the results obtained from electrochemical impedance measurements, surface morphology and cross section profile were observed by scanning electron microscope (SEM). The element composition or distribution was analyzed by EDS. Fig. 6 and Fig. 7 show the surface morphology and the result of EDS analysis for Inconel 600 after two thermal cycles test under molten sulfate film, respectively. It can be seen from Fig. 6 that the surface of Inconel 600 is uniform and no peeling off or severe local corrosion occurred. The elements analysis by EDS proved the formation of oxide (mainly chromium oxide) on the surface of Inconel 600. It is considered that protective chromium oxide formed on the surface prevented Inconel 600 from accelerated corrosion. Even under thermal cyclic condition, the surface oxide film kept its excellent protective property. Results for aluminide diffusion coating are shown in Fig. 8 and Fig. 9. The surface is uniform but rougher than that of Inconel 600. Also, instead of formation of chromium oxide, aluminum oxide was formed on the surface of aluminide diffusion coating



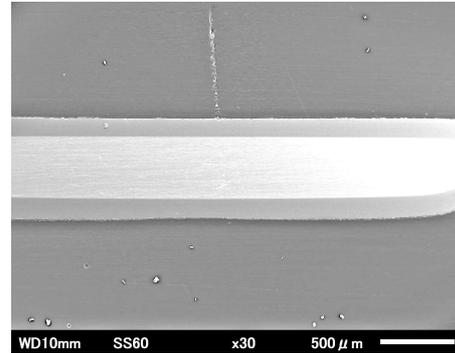
**Fig. 8.** Surface morphology for aluminate diffusion coating on Inconel 600 after two thermal cycles test under molten sulfate film and in air atmosphere.



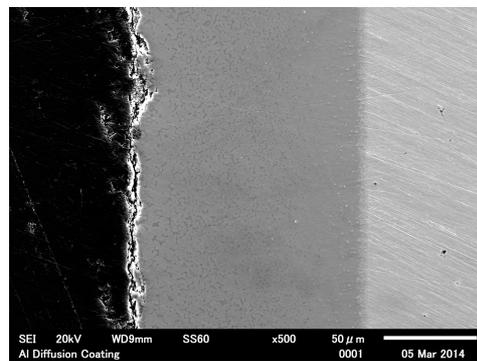
**Fig. 9.** Result of EDS analysis for aluminate diffusion coating on Inconel 600 after two thermal cycles test under molten sulfate film and in air atmosphere.

as shown in Fig. 9. This is well correlated to the impedance behavior showed in Fig. 3. It is also considered that the roughness of the aluminate coating surface resulted in less uniform distribution of molten salt on the surface of coating and therefore caused instability of impedance monitoring.

In the case of aluminate diffusion coatings, the state of coating layer and its adhesion to Inconel 600 substrate are also important to its performance against corrosion. Fig. 10 and Fig. 11 show the cross section profiles for aluminate diffusion coating in different magnification by SEM. It can be seen that aluminate coating layer is uniform and there is no cracks in the coating layer across the whole coating layer (Fig. 10). From Fig. 11, it can be seen that the interface of aluminate coating layer and Inconel 600 substrate is smooth and no obvious defects such pits or cracks were found. Fig. 12 shows the results of element mapping across the aluminate coating layer. The coating layer consists of aluminum, nickel, chromium and iron. Since elements that belong to Inconel 600 substrate also exist in coating layer, it means that inter-



**Fig. 10.** Cross section profile (x30) for aluminate diffusion coating on Inconel 600 after two thermal cycles test under molten sulfate film and in air atmosphere.

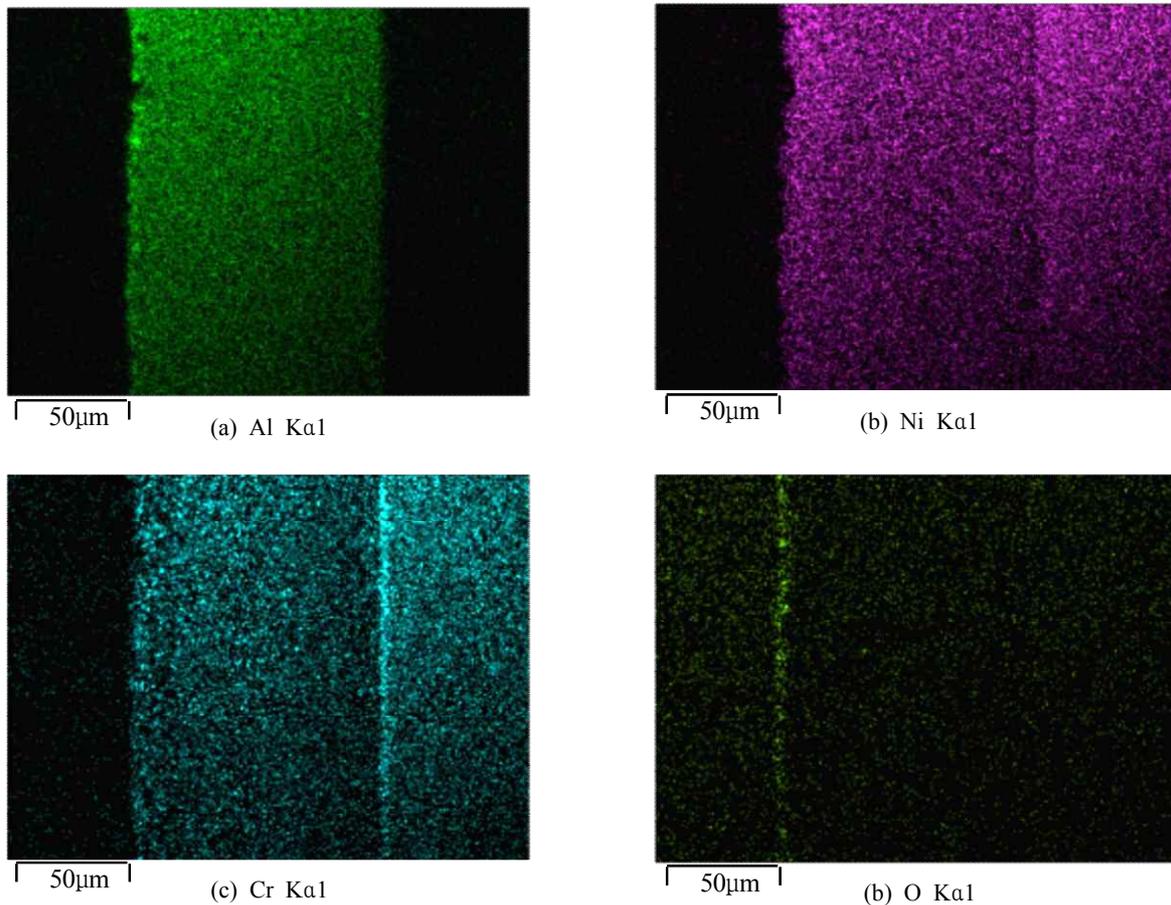


**Fig. 11.** Cross section profile (x500) for aluminate diffusion coating on Inconel 600 after two thermal cycles test under molten sulfate film and in air atmosphere.

diffusion between the elements from substrate and aluminum from coating materials occurred during the diffusion treatment. Oxygen was found on the top of coating layer, meaning the formation of oxide film (mainly alumina) on the surface of aluminate diffusion coating. It is concluded that the results of SEM observation and elements analysis by EDS were well correlated with the monitoring results of electrochemical impedance both for Inconel 600 alloy and aluminate diffusion coatings.

#### 4. Conclusions

The degradation processes of Inconel 600 and its aluminate diffusion coatings under molten sulfate film with thermal cycles were monitored by electrochemical impedance measurements. It was found that corrosion resistance for both materials increased with temperature decreasing. On the other hand, the condition of molten salt was also monitored successfully by measuring the changes of impedance at high frequency. In the case of aluminate diffusion coatings, information for both surface aluminum oxide film



**Fig. 12.** Results of Elements analysis by EDS for the cross section of aluminide diffusion coating layer after two thermal cycles under molten sulfate film.

and the solution resistance were obtained from the impedance at high frequency area. With two thermal cycle testing, both Inconel 600 and aluminide diffusion coatings showed excellent corrosion resistance. Postal SEM observation and EDS analysis were well correlated with the results of electrochemical impedance measurements. Therefore, it is concluded that electrochemical impedance technique is very useful under molten salt film condition even with thermal cycles.

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