



# Inhibiting effect of Ni-Re interlayer between Ni-Al coating and steel substrate on interdiffusion and carburization

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## ABSTRACT

A Ni-Re film was electroplated as a diffusion barrier between the Ni-Al coating and the iron alloy substrate. The interdiffusion between the coating and the substrate was investigated by micro-structure analysis, and the interdiffusion coefficient was calculated using Boltzmann-Matano method. The results indicated that the Ni-Re interlayer played a superior barrier effect, almost fully blocking interdiffusion and retarding the formation of diffusion zone (DZ). The Ni-Al coating without a diffusion barrier showed severe carburization corrosion in the diffusion zone during carburization process, while the Ni-Al coating with the Ni-Re diffusion barrier effectively protected the steel substrate from carbon attack.

## 1. Introduction

Ni-Al coatings are widely used for protecting low protective substrate materials from high temperature corrosion in oxidizing or carburizing atmospheres [1–4]. Early studies showed that the intensive interdiffusion occurred between the coating and the alloy substrate at elevated temperatures [5–9], which rapidly lowers the concentration of Al in the coating even at a relatively low temperature of 650 °C [10]. Since the protective Ni-Al layer cannot be sustained when Al concentration decreases to a certain level, the coating can be destroyed rapidly by the fast corrosion under high temperature service environment [11–13]. Moreover, due to the outward diffusion of alloy elements such as Fe, Cr, etc. and inward diffusion of Al and Ni, a thick diffusion zone (DZ) and enormous detrimental brittle phases of (Fe, Al) and (Cr, Al) intermetallic compounds are formed [14–16]. These detrimental brittle phases in DZ are vulnerable to carburization or oxidation, leading to the deterioration of mechanical properties of the coating and the alloy substrate. Therefore, it is essential to reduce the diffusion zone by restraining the interdiffusion between the coating and the substrate to achieve a long-life protecting effect of Ni-Al coating.

Several types of diffusion barriers, such as ceramic interlayers (Al–Al<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>) [16–18], and metallic interlayer Ni–W [19], have been developed for inhibiting the interdiffusion between the coatings and the alloy substrates. Unfortunately, these coatings retard the interdiffusion in some extent but cannot fully block the interdiffusion. Based on the

thermodynamic stability and desirable compatibility of both Ni–Al coating and iron alloy substrate, a Ni–Re electroplated film was chosen as a diffusion barrier in this work [20,21]. By an integrated approach of experimental characterization and diffusion calculation using Boltzmann-Matano method [22], the role of Ni–Re interlayer on interdiffusion between the coating and the steel and its protection in carburization process was revealed.

## 2. Experimental

### 2.1. Coating preparation

Samples with dimensions of 20 × 5 × 2 mm were cut from steel alloy (the chemical composition is shown in Table 1), then abraded to a final 800 grit SiC paper, and ultrasonically cleaned in acetone. After that, the samples were electrodeposited by a ~10 μm thick Ni–Re layer in a nickel sulfate bath (200 g/L NiSO<sub>4</sub>·6H<sub>2</sub>O, 0.2 g/L C<sub>12</sub>H<sub>25</sub>SO<sub>4</sub>Na, 10 g/L NiCl<sub>2</sub>, 40 g/L H<sub>3</sub>BO<sub>3</sub>) with the addition of 1.68 g/L KReO<sub>4</sub> (Step 1 in Fig. 1). Then a Ni layer with a thickness of ~10 μm was electroplated on the surface of Ni–Re layer in the nickel sulfate bath (Step 2 in Fig. 1). The EDS line scan of the sample after electroplating of Step 1 and Step 2 is also shown in Fig. 1. It reveals that the concentration of Re is not uniform inside the Ni–Re layer, with a high concentration close to the substrate steel but a decreasing Re concentration close to Ni layer. Subsequently, the deposited samples were aluminized at 923 K for 5 h

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**Table 1**  
Chemical composition (wt%) of the steel alloy substrate.

| Elements | Cr    | Ni    | Mn   | Si   | P     | C    | S     | Fe   |
|----------|-------|-------|------|------|-------|------|-------|------|
| Contents | 23.73 | 12.04 | 1.27 | 0.54 | 0.025 | 0.03 | 0.004 | Bal. |

using a conventional pack-cementation in a powder mixture of Al (45 wt%) +  $\text{Al}_2\text{O}_3$  (50 wt%) +  $\text{NH}_4\text{Cl}$  (5 wt%) in an Ar atmosphere (Step 3 in Fig. 1). For comparison purposes, a sample coated with Ni-Al only without Ni-Re barrier interlayer was also prepared by applying the Steps 2 and 3 but without Step 1 in Fig. 1.

## 2.2. Quick carburization experiment

A quick carburization experiment was conducted by packing the samples with the activated carbon nanopowders in alumina crucibles placed in a ceramic tube furnace at 1273 K for 10 h under Ar atmosphere.

## 2.3. Characterization and calculation

All the samples were mounted in the epoxy resin, grinded up to 1500 grit SiC paper, polished up to 1  $\mu\text{m}$ , and ultrasonically cleaned in ethanol before analyzing the cross sectional structure of the samples. The surface phases and morphologies were determined by X-ray diffraction (XRD, Empyrean) and scanning electron microscope (SEM 3400X, 20 kV). The samples were mounted in epoxy resins for the cross-section characterization by back scattered electron images (BSE 3400X, 20 kV) and electron probe microanalysis (EPMA-1720, 20 kV) measurement. Meanwhile the concentration-distance profile of Al component was measured, and interdiffusion coefficient during the packing cementation were calculated by simplifying the samples to the Al-Ni diffusion couple and using Boltzmann-Matano method [22].

## 3. Results and discussion

### 3.1. Coating structure and composition characterization

The surface structures of the raw Ni-Al and Ni-Al/Ni-Re coatings were investigated by the X-ray diffraction (XRD) patterns shown in

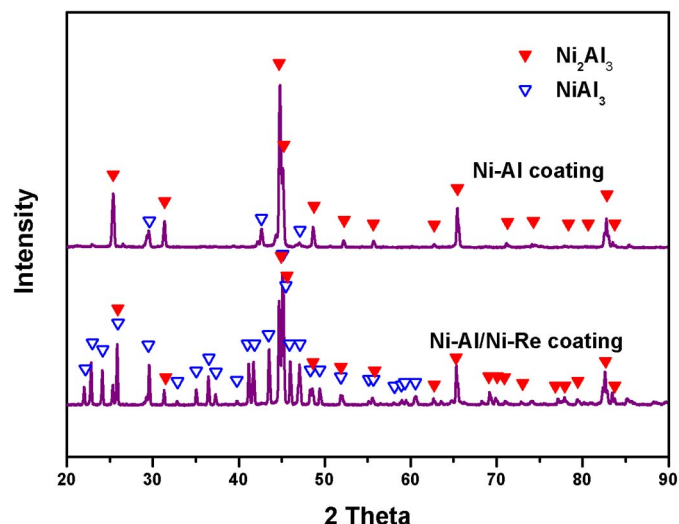


Fig. 2. XRD patterns of the Ni-Al and Ni-Al/Ni-Re coatings.

Fig. 2. It indicates that the outer layer of Ni-Al coating mainly consists of the  $\delta\text{-Ni}_2\text{Al}_3$  phase, in agreement with the study that the Ni film can be converted into a coating of aluminide in its  $\delta$ -phase reported by Tan [23]. While for the Ni-Al/Ni-Re coating, the characteristic peak intensity of the  $\text{NiAl}_3$  becomes much stronger than that of the  $\delta\text{-Ni}_2\text{Al}_3$ , indicating the dominant  $\text{NiAl}_3$  phase on the coating surface. According to the Ni-Al phase diagram [24], the  $\text{NiAl}_3$  phase delays to transform to  $\delta\text{-Ni}_2\text{Al}_3$  when the concentration of Al constantly maintains a high level at the temperature below 1127 K, which indicates the diffusion of Al is depressed in the case of Ni-Al/Ni-Re coating.

The cross-sectional microstructures of the Ni-Al coating and Ni-Al/Ni-Re coating were investigated by BSE images shown in Fig. 3. A thin layer of  $\text{Ni}_2\text{Al}_3$  ( $\sim 20\ \mu\text{m}$ ) and a thick DZ ( $\sim 60\ \mu\text{m}$ ) were observed in the Ni-Al coating (Fig. 3a). It indicates that severe interdiffusion occurs between the Ni-Al coating and the steel substrate. The compositions of the various phases in DZ were detected by EPMA (see the inset image in Fig. 3a) and are listed in Table 2. It can be seen that three phases (grey phase, light grey phase and dark grey phase) formed in DZ during the Al-pack cementation process. All these three phases have high contents

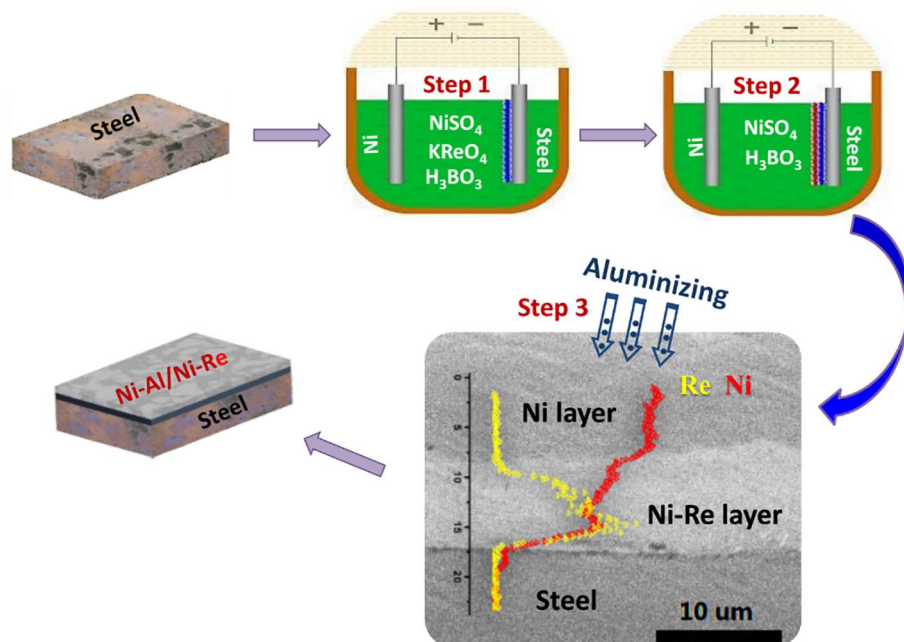


Fig. 1. Schematic illustration of the Ni-Al/Ni-Re coating preparation.

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