Ni-Al phase transformation of dual layer coating prepared by pack cementation and electrodeposition

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Abstract. In this work, Fe-Cr alloys were coated via Aluminum (Al) pack cementation, followed by Nickel (Ni) electrodeposition. The process of pack cementation was done with mixing powders of Al, Al₂O₃ and NH₄Cl with weight percentage of 15%, 85%, and 5% respectively. To control successful Al diffusion to the substrate, pack cementation was conducted for 7 hours with two holding temperatures treatment at 400 °C for 4 hours, and 800 °C for 2 hours. Subsequently, the electrodeposition of Ni was applied with the solution consisting of NiSO₄, H₃BO₃, and NiCl₂. The samples were placed in the cathode, and then dipped in the solutions, while Ni plate used as anode. Successfully the samples were coated by dual Al-Ni layers, the samples were slowly heat treated at 900 °C for 10 hours. The inter-diffusion of Al and Ni were characterized with SEM/EDX to investigate the distribution of the elements. Mechanical properties of the coated substrates were analyzed with Hardness Vickers (HV). It was found the hardness of the substrate increased significantly, from originally 255 HV to the 1177 HV after pack cementation. The hardness of the substrates has decreased to 641 HV after Ni plating, but subsequent heat treatment has been able to increase the hardness to 842 HV. This phenomenon can be correlated to the inward Al diffusion, and outward Fe, Cr diffusion. The formation of intermetallic compounds due to Al inward and Fe, Cr outward diffusion were discussed in details.

1. Introduction
Nickel aluminide (NiAl) has been considered as a promising alloys for high temperature applications after exhibiting high melting point, high corrosion and oxidation resistance, and high hardness and ductility [1, 2]. There are at least five stable intermetallic compounds found from NiAl alloys namely NiAl₃, Ni₂Al₃, NiAl, Ni₂Al₅, and Ni₃Al. The formation of those intermetallic compounds corresponds respectively with the atomic compositions. Among mentioned compounds, NiAl and Ni₃Al are considered to having desirable properties, and respectively known as β and γ’ phases. Despite that NiAl and Ni₃Al have been reported to have better oxidation resistance, high specific strength, combined with high hardness, and high electrical conductivity, the application of those compounds are still limited due to poor ductility at room temperature [3].

In incorporating NiAl compounds on the surface of the engineering alloys such as stainless steels has been becoming a major investigation recently. Stainless steels are widely used for many industrial applications, especially for the alloys with Fe-Cr as major constituents. Fe-Cr exhibits good oxidation resistant, however with the increasing operating temperature, the oxidation rate increase significantly mainly caused by water vapors [4-6]. In this paper, Fe-Cr with chemical compositions shown in table 1 is used as the substrate. The aim of the study is investigating the diffusion characteristic of the
constituent elements, especially Fe, Cr, Ni, and Al in the substrate due to dual Ni-Al coatings. This paper also identifies the hardening mechanism of the substrate after Al pack cementation, and different hardening mechanism after Ni electroplating and heat treatment.

Table 1. Chemical composition of Fe-Cr alloys as the substrate (in atomic %)

|   | Fe   | C    | Cr   | Ni   | Mo  | Mn  | Co  | Si   | Other as Impurities (P, S) |
|---|------|------|------|------|-----|-----|-----|------|---------------------------|
|   | balanced | <0.08 | 16-18 | 10-14 | 2-4 | 2   | 1   | Max 1 | Max 1                     |

2. Experimental procedures

The samples were cut to the dimension of 9.3×20.2×3 mm, and then the surface were ground with sandpapers of 1000 SiC grit to remove the scratches and oxidation on it. The sample was further cleaned with acetone and dried up with hot air. There were 4 samples kept in Al₂O₃ crucible, and then dipped with pack cementation powder consisting of Al, Al₂O₃, and NH₄Cl, respectively with 15%, 85%, and 5% weight ratio. The crucible was closed and sealed with concrete and then kept at the room temperature for 2 hours allowing calcination to occur. The vacuum furnace was prepared with the heating rate of 5 °C/min. When temperature inside the vacuum reached 400 °C, the temperature was hold for 4h. Subsequently the temperature was increased until 800 °C with the same heating rate and then holds it again for 2h. The sample was kept in the vacuum furnace until it cooled down.

![Figure 1](image-url) (a) Illustration of pack cementation process. The samples were dipped in the mixing powders, heat it for 7 hours with two holding temperature at 400 °C for 4 h, and 800 °C for 2 h. (b) The appearance of the sample before and after pack cementation.

After the sample was aluminized, the Ni electroplating was prepared with the solution of NiSO₄, NiCl₂, H₃BO₃, having weight portion of 165 gr, 22.5 gr, and 20 gr respectively. The sample was put on the cathode, and the nickel plate was on the anode. The current density for the Ni plating was 20 mA/cm². The heat treatment was done for 10 to allow complete reaction between Al and Ni. The microstructures were investigated with Scanning Electron Microscopy (SEM) Hitachi SU-3500 equipped with Energy Dispersive X-ray (EDX) to investigate the element distributions. The micro hardness was conducted with automatic LECO LM 100AT to measure substrate, surface after pack cementation and heat treatment.

3. Results and discussion

The microstructures of the sample after pack cementation and Ni-plating and heat treatment are shown in figure 2. Figures 2a and 2b, respectively, correspond to the after Al pack cementation and Ni electroplating and heat treatment for 10 h. The grains produced by Ni plating and heat treatment are finer than the one produced by pack cementation. The hardness of the sample was measured and we obtained 1177 HV after pack cementation, which is very hard as compared to the original substrate at
around 255 HV (figure 3). The hardness after pack cementation strongly indicates the formation of Fe-Al intermetallic compounds. Intermetallic compounds of Fe-Al were summarized by Potesser et al [7], among which the most hardness of the compounds found from Al rich to form Fe$_2$Al$_5$ with orthorhombic crystal structure and the hardness may reached over 1000 HV [8-9]. The hardness of the sample after Ni-plating and subsequent heat-treatment for 10 h were measured at 641 HV and 842 HV, respectively. The cross-section of the substrate after two coatings can be seen in figure 4. The thickness of the coating from Al pack cementation is 124 µm, while the double coating layers of additionally Ni-plating has the thickness of 153 µm.

There is inter-diffusion zone (IDZ) obtained from Al pack cementation, which the thickness is 25.1 µm figure 4b. Above IDZ is Al matrix with intermetallic compounds act as the solid solution hardener, which is identified as white flakes. Further coating with Ni has produced additional layer with thickness of about 21 µm, with second IDZ thickness is about 11.7 µm. From the cross section of the substrate, there are cracks formed in the interface between Al matrix and the outer-zone, near the surface. The cracks are pronounced significantly after Ni-plating and heat treatment, which could be influenced by the different of the thermal expansion coefficient.

Figure 3. The hardness of the sample is 1177 HV after pack cementation, which is very hard as compared to the original substrate at around 255 HV.
The mapping of element diffusions is shown in figure 5 for the substrate with Al pack cementation. The specific interest is observing the distribution of Fe, Al, and Cr through the cross-sectional substrate. In general, Al is found on the top of substrate, while Fe and Cr are concentrated mainly in substrate with few atoms are distributed in the top layer. Interesting to note, the inward diffusion of Al is not seen from figure 5b. This indicates that IDZ has been formed to prevent any Al diffusion to the substrate.

Further mapping analysis is carried out from the cross section of the substrate after dual coatings, which produce significant cracks between Al and Ni matrixes as shown in figure 6a. The mapping of element Oxygen (O) is strongly concentrated in the crack region as shown in figure 6b. This indicates the large portion of porosity is created, which could disrupt the mechanical properties of the substrate.

**Figure 4.** (a) The cross section of the substrate after Al-pack cementation, and Ni electroplating plus heat treatment. The thickness of the coating layers is 153 μm. (b) The cross section of the substrate after Al pack cementation, the thickness of the layer is 124 μm.
Figure 5. The elemental mapping from the cross section of the substrate (a), indicating Al rich on the top layer, while the Fe and Cr are distributed mainly in the substrate as shown in (c) and (d).

Figure 6. (a) The mapping of the cross section of the substrate, and (b) the porosity is created in the cracks area that was produced from the Al pack cementation.

Further mapping analysis is carried out to observe the diffusion behavior of the atoms after dual coatings, as shown in figure 7. Element of Cr and Fe are mainly distributed on the substrate up to the Al coating. Interesting to note, there are no Fe and Cr outward diffusion through the IDZ that is formed between Al and Ni matrix. The hardness was measured after Ni-plating and heat treatment in the range of 600-850 HV, which correspond well to the hardness of NiAl intermetallic compounds [10]. Further Ni deposition via electroplating has produced IDZ, which could prohibit the outward diffusion of Fe and Cr. This is very important finding because any outward elemental diffusion will create microstructure instabilities of the substrate, as it has been proved by Watson et al. and Locci et al. in different materials [10-12].
The formation of Fe-Al intermetallic compounds could act as the diffusion layer if the substrate is exposed at elevated temperature and Oxygen environment. It is expected that Al$_2$O$_3$ layer will be formed, and Al could act as a container to prevent outward diffusions of the elements from the matrix. Further analysis is needed to statistically investigate solid solutions and distribution of every element in the sample.

4. Conclusions
From this work, it can be concluded that Al pack cementation is effective to increase the hardness of the substrate. The hardening mechanism can be correloated to the formation of solid solutions such as Fe$_2$Al$_5$, which is strongly identified by high micro-hardness that reach 1077 HV. The second layer produced by Ni electrodeposition could act as the barrier for the Fe and Cr outward diffusions. The hardness of the substrate after dual coatings is reduced to the 844 HV. This investigation is a first step to develop protective layer Al$_2$O$_3$ that could improve oxidation resistance of Fe-Cr alloys.

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Figure 7. (a) Elemental mapping of Ni is concentrated in the top layer, while Cr (b) and Fe (d) are distributed on the substrate and Al matrix (c).
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