Effect of the Mechanical Properties and Corrosion Behaviors of Nickel-Cadmium Duplex Electroplated AISI 4340 Steel by Using Various Solid Solution Treatments

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AISI 4340, a high strength low alloy steel employed in aeronautical structural components, are always protected by various surface treatments from failure. In order to obtain better mechanical properties and corrosion resistance economically, in this study, multiple surface treatments were applied to the AISI 4340 steel, including of nickel-cadmium duplex electroplating, chromate conversion processing, and solid solution treatments with different temperatures and duration times. To evaluate the properties of the nickel-cadmium duplex coating for various solid solution treated AISI 4340 steel, thickness and hardness measurements, salt spray tests, XRD and SEM inspections were performed.

The experimental results showed that the electroplated specimens, followed by 300–350°C solid solution treatment, exhibited a distinct nickel-cadmium intermediate compound (Cd5Ni). The highest hardness reached was HV0.3 582.9 after 300°C solid solution treatment for 120 min. Moreover, the anti-salt corrosion capability of the nickel-cadmium layers effectively improved with the 300–325°C solid solution treatment. However, the mechanical properties and corrosion resistance declined with the increase in temperature above 350°C because of the depletion of the cadmium layer and Cd5Ni compound, and the formation of cadmium oxide and chloride.

1. Introduction

Since 1970's, high strength low alloy steel, e.g. AISI 4340 steel, has been designed for the highly critical buffer and transmission parts in commercial and military aircraft because of its admirable strength and toughness. For example, the articles in Boeing 747 series aircraft, such as flip actuators, gimbal fittings, landing gears, etc., make contribution to only 5–15% of the airframe structural weight but serve to provide more than 700 MPa of tensile strength.1)

Due to the electrochemical vulnerability of high corrosion activity of bare AISI 4340 steel in atmosphere, many surface treatments, including plating, anodizing and painting processes have been applied. Among these processes, electroplated cadmium layers possess excellent corrosion resistance, low thermal expansion, good lubricity and galvanic compatibility with different metals. According to the previous academic literatures2,3) and aeronautical manufacturers’ specifications4,5), cadmium coating as a sacrificial protective layer on steel surface has been served since the first description about its cyanide plating solution in 1849.6) The cadmium electroplate processes have still progressively been developed and performed as the essential surface treatment procedures for military and commercial aircraft parts since 1930's.6) Because the toxicity of cadmium and its compounds jeopardize global environment and ecosystem, many alternative depositions, such as zinc, zinc-nickel, and tin-zinc electroplating have exploited.7,8) However, the physical and anti-corrosive properties of zinc and its compounds, heretofore, have not been equivalent to cadmium coatings for aerospace industry requirement.9) Therefore, cadmium and its relevant electroplating technologies still ineluctably applied on some AISI 4000 series steels.10)

Although cadmium plating has still been irreplaceable in some fields of industry, in the plating process, the overpotential of hydrogen in cathode can initiate the formation of considerable quantities of hydrogen clusters. These hydrogen compounds are prone to be trapped and hibernated onto the interfaces between coating layer and base material. Going through their nucleation, growth, and then accumulation, hydrogen embrittlement or hydrogen assisted cracking eventually takes place, as investigated by D. Herlach et al.11,12) Therefore, a further improvement of cadmium plating process is required.

On the other hand, the electroplating nickel layer has outstanding corrosion and wear resistance in respect of industrial applications.13,14) Nickel coating can be served as a barrier between different metals to prevent unfavorable elements from migrating and diffusing among different alloys, which may preclude the development of galvanic corrosion. Because of its distinguished adhesive strength and ductility, nickel layer also has usually used as the protective buffering intermediate between protective coating (e.g. hard chromium layer) and ferritic substrate material in airframe structure.15)

Actually, the previous papers studied about the effect of multiple electroplated high strength low alloy steel were rare. Therefore, in this study, the mechanical properties and anti-corrosion effects of nickel-cadmium duplex electroplated AISI 4340 steel under different surface treatments are need to further investigated. The aim of this work was to explore a series of solid solution treatments for nickel-cadmium duplex electroplated AISI 4340 steel in order to examine the effects on the mechanical properties and corrosion behaviors of nickel-cadmium-strengthened 4340 steels.

2. Experimental Procedures

In industry, electrodeposited cadmium regarded as an excellent sacrificial protective layer on steel surfaces. Nickel coating between plated cadmium and a substrate alloy (AISI 4340 steel) effectively enhances the strength of a substrate material. Nickel-cadmium duplex electroplating layers could form certain anti-corrosive intermediate products after spe-
sific solid solution treatments. In the research, rectangular-shaped AISI 4340 steel samples were prepared with two different dimensions: 100 mm (L) × 25 mm (W) × 1 mm (T), and 150 mm (L) × 100 mm (W) × 1 mm (T), respectively (19 pieces of coupon in each). All the samples underwent stress relief by heat treatment at 190°C for 4 h sequentially, fastened in fixtures and cleaned by both degreasing and grit-blasting processes. All the specimens were continually processed by nickel plating in a sulfamate bath at 0.033 amp-cm⁻² for 15 min, followed by cadmium plating in a cyanide bath at 0.027 amp-cm⁻² for 15 min. Hereafter, these coated specimens were rinsed and dehydrated. Eventually, these specimens obtained final average thicknesses in the range of 7–8 µm for nickel and 6–7 µm for cadmium layers. Tables 1 and 2 show the ingredients of the nickel plating and cadmium plating solutions, respectively. The chemical composition of AISI 4340 steel as shown in Table 3.

For each sample, there was a plated specimen classified as a 'control group' which was not used in any heat treatment. The other 18 pieces, an "experimental group", were separated into 6 equal sets (3 pieces/set) and underwent solid solution treatments in a muffle furnace at 275, 300, 325, 350, 375 and 400°C, respectively. For each temperature level, there were three different durations of time (30, 60 and 120 min). Each specimen only baked at a certain temperature for a certain time duration. Afterwards, all the specimens underwent a chrome conversion coating treatment with 8 vol% diluted chromium trioxide conversion concentrate for 10 s and were then rinsed in deionized water and dehydrated. Eventually, these specimens obtained final average thicknesses in the range of 7–8 µm for nickel and 6–7 µm for cadmium layers. Tables 1 and 2 show the ingredients of the nickel plating and cadmium plating solutions, respectively. The chemical composition of AISI 4340 steel as shown in Table 3.

Second, the salt spray test applied to specimens measuring 150 mm (L) × 100 mm (W) × 1 mm (T) in accordance with ASTM specification B117-11. The concentration of salt in the deionized water was 5 mass%, the operational pressure range was 9.8 × 10⁻² MPa, the operating temperature was 35°C and the duration time was 120 h. When the test completed, in order to prevent existed corrosion from further propagation, all specimens had to be cleaned with deionized water to remove the salty residue as soon as possible; they were then dehydrated.

Finally, all specimens would be examined by SEM (Hitachi-S4700), and used the line scan analyses to evaluate the relation between solid treatment conditions, the texture/configuration of cadmium-nickel duplex-coated layers, and their mechanical/anti-corrosion properties.

3. Results and Discussion

The hardness trend of nickel-cadmium layers using different solid solution treatments as shown in Fig. 2(a). Significantly, for solid solution treatments at 275 and 300°C, the hardness of the nickel-cadmium layers increased steadily with the increased duration of time. The three highest hardness values were HV₀.₃ 582.9 at 300°C/120 min, HV₀.₃ 579.9 at 325°C/60 min and HV₀.₃ 571.9 at 350°C/60 min, respectively. Generally, the higher hardness resulted from the formation of multi-intermediate phases (Cd₅Ni) in the nickel-cadmium boundaries, as illustrated by the phase diagram of nickel-cadmium alloys. From 350 to 400°C, the...
hardness of the nickel-cadmium layers decreased with the increased duration of time because of the dissipation of the protective intermediate coatings and the subsequent propagation of brittle CdO. The softness of the nickel layer resulted from the re-crystallization and growth of nickel grains, which was consistent with the investigations by C. Lin et al. 17)

Notably, an interesting hardness distribution dramatically found within the nickel-cadmium coated onto the AISI 4340 steel substrate by different solid solution treatment temperatures. Although the specimen at 325°C/60 min did not acquire the maximum hardness value, it maintained the hardness of AISI 4340 steel substrate to HV0.3 299.7 below the 40 μm of nickel layer. However, at the same position, the hardness value was only HV0.3 243.8 after solid solution treatment at 300°C/120 min, as shown in Fig. 2(b). Therefore, it is reasonable to suggest that the optimal hardness value and distribution were achieved through solid solution treatment at 325°C/60 min.

Figure 3 shows the XRD patterns of the duplex electroplated specimens after various solid solution treatments. From 275 to 375°C, the intensities of Cd5Ni at all treatment duration times were obvious. Above 350°C, this intensity began to decrease as the treatment temperature and duration times increased. The Cd5Ni almost completely dissipated at 400°C/120 min. It is reasonable to assume that the melting point of Cd5Ni is approximately 400°C, in accordance with the binary phase diagram of cadmium and nickel. 16) In the Cd and Cd5Ni binary system, the phase transformation of Cd5Ni samples, heated from 275 to 400°C consists of peritectic and liquefaction reactions. The reactions are as follows:

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\text{Cd(s)} + \text{Cd5Ni(s)} \rightarrow \text{Liquid} + \text{Cd5Ni(s)} \quad \text{at 318°C} \quad (1)
\]

\[
\text{Liquid + Cd5Ni(s)} \rightarrow \text{Liquid} \quad \text{at 400°C} \quad (2)
\]

There was an obvious trend in each heating duration time - the intensity of CdO increased with the ascending temperature, especially at 350, 375 and 400°C. In the XRD patterns after 60 and 120 min, the increase in CdO and the decrease in Cd5Ni were simultaneous, as shown in Figs. 3(b) and (c). This phenomenon might result from the hot oxidation of cadmium and dissipation of Cd5Ni. According to the discussion and results aforementioned, it is reasonable to speculate that below 325°C, every alloy element (except Cd5Ni) in the coating layer was dormant. From 325 to 375°C, the beneficial components, such as Cd5Ni, were dominant in the microstructure of electrodeposition. Above 375°C, the CdO evidently formed and corrosion in the nickel-cadmium layers began.

In the present research, a stronger vanadium signal also found in the XRD pattern at 400°C, and the intensity in vanadium increased with the increase in solid solution treatment time. In electroplating, vanadium was probably ionized from the anodic basket (was made of Ti-6Al-4V alloy) since the electrochemical activity of vanadium is closer to that of cadmium than titanium or aluminum. Thus, it seemed necessary to reduce the interference from irrelevant elements and maintain the accuracy of our experiments.

Figure 4(a) illustrates the texture and composition distribution of nickel-cadmium duplex coating layers by SEM.
and line scan analysis. As seen in Fig. 4(a), there are obvious cadmium, nickel and iron elements (as indicated by the arrows) distributed on the nickel-cadmium duplex coating layers. Besides, there is no delamination and transverse separation between the interfaces of cadmium, nickel coating layers and steel substrate, which indicates the superior dense bonding adherence of the multiple layer structure. In this photograph, cadmium film shows the characteristic of porosity, in which the detrimental hydrogen, formed during plating process, could escape after a proper baking procedure. This specimen was not processed any solution treatment and only served as a sample of control group. Among the other specimens with various solid solution treatments (experimental group), after the process of salt spray test, the chrome conversion coating, cadmium and nickel layers began to appear different levels of disintegration, which was obviously at higher temperatures (above 350°C) and longer duration time (60 and 120 min). In the aforementioned temperature range, the line scan analysis disclosed the corrosion reaction configurations at 400°C/120 min as shown in Fig. 4(b). Considerable cadmium was seriously dissipated, only the nickel could maintain the coating layer. The small amount of oxygen and chlorine came from the solid solution treatments and salt spray test respectively. These foreign elements eventually formed cadmium oxide and chloride, as indicated by the arrows in Figs. 4(b) and 9(f).

On the other hand, Fig. 5 shows the OM observation of nickel-cadmium duplex electroplated steel after solution treatments in 30 min at various temperatures. This result clearly indicates that microstructures in the nickel-cadmium layer and AISI 4340 steel substrate were stable and distinct from 275 to 350°C. The phase diagram of nickel-cadmium alloys can demonstrate this phenomenon.16) In the cadmium-rich zone, between 275 and 350°C, solid Cd₅Ni and semi-liquid cadmium formed a phase of stable peritectic Cd₅Ni. Above 375°C, part of the peritectic Cd₅Ni might also be liquefied; the microstructure of the electrodeposition layers and AISI 4340 alloy substrates would be degraded. As R. Weil et al. pointed out, solid nickel cannot maintain its strength if the heat treatment temperature is above 400°C.18)

In addition, the thicknesses of the coatings at 325, 350, 375 and 400°C descend obviously (below 4.1 μm) in the first 60 min, as shown in Fig. 6(a), which could result from the liquefaction and dissipation of cadmium, because the melting point of cadmium is approximately 321°C. The remainder of cadmium, below 318°C, would form Cd₅Ni layers with the solid nickel nearby, with a peritectic reaction. On the other hand, the thickness of the nickel layer remains at a stable constant in the first 60 min (below 375°C), as shown in Fig. 6(b). However, the thickness descends obviously (below 4.2 μm) in the first 30 min (above 350°C), probably due to both the formation of the intermediate phase Cd₅Ni and the solid solution with γ-iron.16)

Figures 7 and 8 reveal the results of the macroscopic configurations of nickel-cadmium duplex coated layers before and after salt spray test. As shown in Figs. 8(a)–(c), cadmium layer was still solid and thoroughly adhered to nickel coating and the intermediate phase of Cd₅Ni easily formed, which can be interpreted by the XRD patterns in accordance with Fig. 3. As a result, the protective layer was uniform and untainted. It is reasonable to suggest that the capability of corrosion resistance within the temperature range (300–325°C) was excellent. Conversely, when the temperature rose to 375°C, micro-cracks began appearing between the clusters of cadmium coating and propagated with the increase of treatment time, eventually; the cadmium layer precipitation was falling down in 400°C, as shown in Figs. 9(d)–(f). In the present research, the chrome conver-
sion coating was almost vanished and the chloride was found on the coating layers within the temperature range between 375 and 400°C.

In addition, Fig. 8 shows the surface morphology observations of salt spray results of nickel-cadmium duplex electroplated AISI 4340 steel after various solid solution treatments in accordance with Fig. 8. Among the SEM photos, Figs. 9(a)–(c) represent that the main protective layer (cadmium) was still obviously reserved on the substrate after 300 and 325°C solid solution treatments. However, Figs. 9(d)–(f) reveal that the cadmium coating began to crack and segregate, and the cadmium oxide and chloride on scratch groove were formed above 350°C, in which the cadmium layer was in process of disintegration. Actually, the nickel layer was able to continually integrate and prevent the corrosion from extending to AISI 4340 steel substrate. This result is consistent with Fig. 8. Consequently, the specimens treated with a 375–400°C solid solution possessed relatively low corrosion resistance.

4. Conclusions

In this work, the solid solution temperature seemed to be a critical parameter for the hardness of duplex electroplated specimens. The hardness test results showed that the softness of nickel was owing to the change in the nickel structure when the solid solution temperature exceeded 400°C.
XRD analyses also indicated that if the treatment temperatures were higher than 350°C, the intensity of the intermediate phase of Cd₅Ni would quickly decrease. Therefore, to acquire smooth and stable coated layers with a beneficial intermediate phase Cd₅Ni, the solid solution treatment temperatures should be in the range of 300–350°C.

These corrosive behaviors confirmed by the results of a salt spray test. The SEM and line scan analysis disclosed that, at 375 and 400°C, the residual chrome conversion coating and cadmium, i.e., intermediate phase Cd₅Ni, was not effectively protective. The corrosion products, i.e. cadmium oxide and chloride, continually formed and eroded the coating layer. Only did the nickel layer play the main role to maintain the mechanical and anti-corrosion capability. In order to achieve an optimal anti-corrosion effect, solid solution treatment at 325°C/60 min is recommended. The procedure created excellent hardness stability in the Cd₅Ni compound, but little generation of cadmium oxide.

Acknowledgments

The experimental specimens and electroplating equipment are supported by the Repair Section 1, Department of Engine Maintenance, Division of Maintenance, CHINA AIRLINES LTD.

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