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Properties of Nickel-Coated Steel Sheets for Battery Case

Takehiro TAKAHASHI* Kiyokazu ISHIZUKA
Koji KAWANISHI

Abstract

Ni-coated steel sheets were used for several battery cases, as Ni has an excellent chemical resistance. As Ni-coating provides barrier corrosion protection and doesn't provide galvanic corrosion protection for steel sheet like Zn coating, corrosion resistance of Ni-coating for steel sheet gets worth when Ni-coating contains some pin holes and cracks. Therefore, we developed SUPERNICKEL™ as a high performance Ni-coated steel sheet to avoid adverse effects of pin holes and prevent the occurrence of cracks at forming. Corrosion resistance of SUPERNICKEL™ is better than ordinary Ni-coated steel sheets, especially after forming, as SUPERNICKEL™ has higher flexibility Ni layer than ordinary electrodeposited Ni layer and has good adhesion by Fe-Ni alloy layer which is formed by diffusion between Ni layer and steel sheet.

1. Introduction

Owing to the excellent chemical resistance of Ni, Ni-coated steel sheets are widely and mainly used as battery case material of alkali manganese dry, lithium-ion and Ni metal-hydride batteries (**Fig. 1**). Furthermore, by taking advantage of the heat resistance that Ni has, Ni-coated steel sheets are also used for heated members of cooking appliances. Ni-coated steel sheets of "SUPERNICKEL™" of Nippon Steel & Sumitomo Metal Corporation are also widely employed for such use.[1)]

As the method of coating Ni for battery cases, there are two methods: coating the entire case after forming and coating a coiled sheet before forming. In Ni-coating after forming, it is difficult to obtain uniform coating on the inside surface of a case, but if the Ni-coating is applied before forming, forming of uniform Ni-coating on the inside surface of a case is possible and stabilized product quality is realized. On the other hand however, when Ni-coating is applied before forming, cracks may be developed in the Ni-coating layer due to forming. Ni-coating is of the barrier corrosion protection type that lacks sacrificial corrosion protection effect like that of Zn, sometime pinholes and/or cracks that exist in the coating layer deteriorate corrosion resistance remarkably.[2)] Therefore, SUPERNICKEL™ was developed, which is intended for avoiding the adverse effect of pinholes and for the suppression of cracks.

Conventionally, in many cases, electroplated steel sheets are produced by the electroplating of an annealed steel sheet coil after cold rolling, as shown by the lower process in **Fig. 2**. On the other hand, as shown by the upper process in Fig. 2, SUPERNICKEL™ is produced by providing electroplating to a steel sheet coil after cold rolling and before annealing, and then, by annealing the coated coil. **Figure 3** shows the schematic of the cross sections of Ni-coated steel sheets produced by the two processes. By forming a diffusion alloy layer of Fe-Ni on the interface of the steel sheet and the Ni-coat layer,[3)] adhesion between the steel sheet and the coating layer is improved. Furthermore, the coating layer is softened by the grain size growth along with the change from the electrodeposition structure to recrystallization structure during annealing, as shown in **Fig. 4**.[4)] Furthermore, as **Fig.**

Fig. 1 Examples of the use of SUPERNICKEL™

* Senior Researcher, Hirohata R&D Lab.
1 Fuji-cho, Hirohata-ku, Himeji City, Hyogo Pref. 671-1188

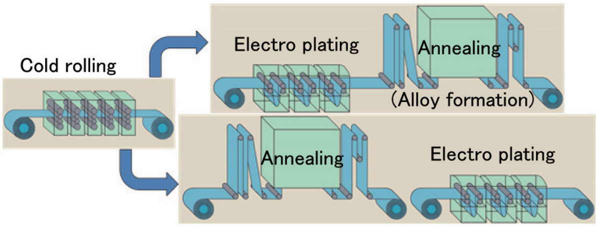

Fig. 2 Production process of Ni-coated steel sheets (above: SUPERNICKEL™, below: ordinary Ni-coated steel sheet)

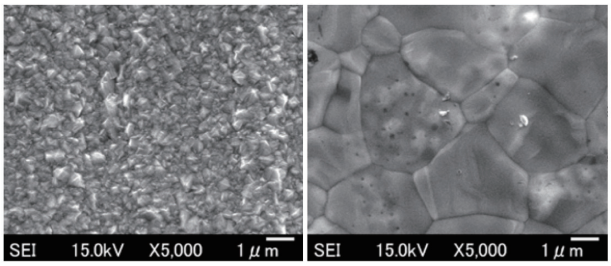

Fig. 4 SEM images of Ni-coating surfaces (left: before annealing, right: after annealing)

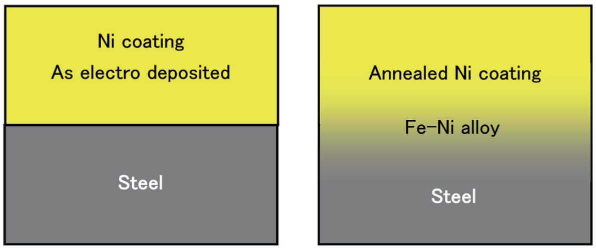

Fig. 3 Schematic diagrams of cross section of Ni-coated steel sheets (left: Ni-coating after annealing, right: Ni-coating before annealing)

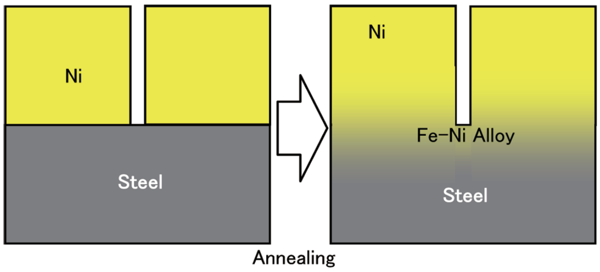

Fig. 5 Schematic diagrams of coating pin pole (left: before annealing, right: after annealing)

Table 1 Test piece

No.	Coating amount		Process		Note
	17.8 g/m²	900 g/m²	1st	2nd	
1	○	○	Annealing (20 s)	Ni-coating	Common Ni-coated steel sheet
2	○	○	Ni-coating	Annealing (20 s)	Equivalent to SUPERNICKEL™
3	–	○	Ni-coating	Anealing (9 h)	For interface analysis

5 shows, annealing after Ni-coating has the effect of avoiding the adverse effect of pinholes in Ni-coating. In the state of Ni-coated, the steel sheet of the substrate material remains as it is at the bottom of a pinhole; however, in case of annealing after Ni-coating like the case of SUPERNICKEL™, the bottom of the pinhole becomes Fe-Ni-alloy-phased. Owing to these basic properties, SUPERNICKEL™ exhibits excellent postforming corrosion resistance.

In this report, the mechanism that improves the postforming corrosion resistance of SUPERNICKEL™ vs. that of the conventional Ni-coated steel sheets is explained in detail, incorporated with the results of tests.

2. Method of Experiment

2.1 Sample preparations

Samples as shown in **Table 1** were prepared. No.2 is the sample that corresponds to SUPERNICKEL™. Two kinds of samples having the Ni-coating weight of 17.8 g/m² and 900 g/m² were prepared, and the sample with the coating weight of 900 g/m² was used only for measuring hardness. Furthermore, No.3 was prepared for examining the alloy layer formed on the interface of the Ni-coating layer and the steel sheet in greater detail, and it was a sample with Ni-coating weight of 900 g/m² alone, and a thick alloy layer was formed by annealing for 9 h. Watt's solution as shown in **Table 2** was used. A Ni sheet was used for the anode, and the cathode current density was maintained at 20 A/dm². The substrate steel sheet was an ultralow carbon steel sheet of 0.25 mm thickness and annealed at 800°C for 20 s.

Table 2 Solution composition

	Concentration (g/dm³)
$NiSO_4 \cdot 6H_2O$	240
$NiCl_2 \cdot 6H_2O$	45
H_3BO_3	35

2.2 Test methods

To confirm the phase structure of the Ni-coting layer, a Ni-coated steel sheet was embedded into resin in the vertical direction and the reflected electron image (COMPO image) from the cross section of the sample was taken by a field emission scanning type electron microscope (FE-SEM) (JEOL JSM-7000F). Hardness of the Ni-coating layer was measured on the sectional surface of a Ni-coated steel sheet embedded in the resin in the vertical direction by a Vickers hardness meter with the load of 49 mN.

To confirm the formability of the Ni-coated layer, a Ni-coted steel sheet was bent by 180° with a sheet of the same thickness, 0.25 mm, inserted in between (1T bending), as shown in **Fig. 6**, and the secondary electron image (SEI image) of cracks on the cross section of the sample was also taken by the FE-SEM. Furthermore, a case of 15 mm in diameter and 40 mm in height was formed by a five-stage stamping, and the corrosion resistance was evaluated. Evaluation of the corrosion resistance was based on the salt spray testing (SST) pursuant to JIS Z 2371. Furthermore, to confirm the state of Ni-coating of the case, a surface analysis of the outer side surface of a case was conducted by an electron prove micro analyzer (EPMA) (JEOL JXA-8230).

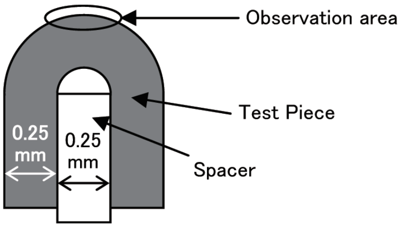

Fig. 6 Schematic diagram of bending test

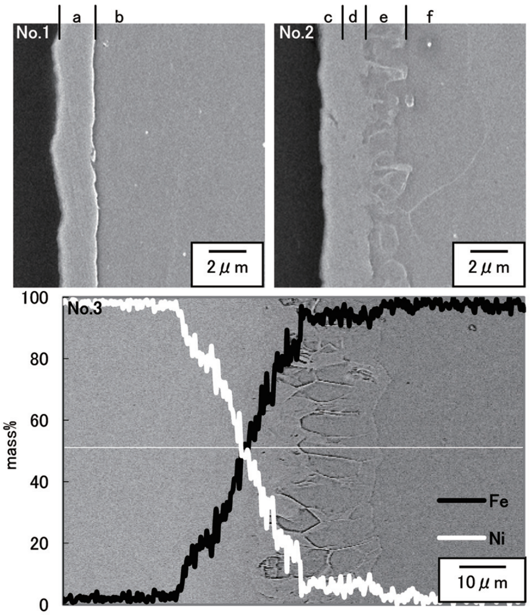

Fig. 7 Cross section SEM images of Ni-coatings

Table 3 Hardness of Ni-coatings (10-points average)

	Hardness (HV 49 mN)
Before annealing	231
After annealing	120

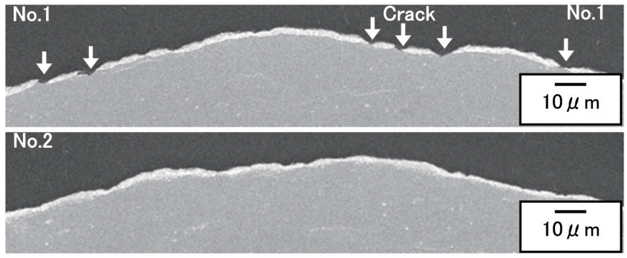

Fig. 8 Cross section SEM images after bending

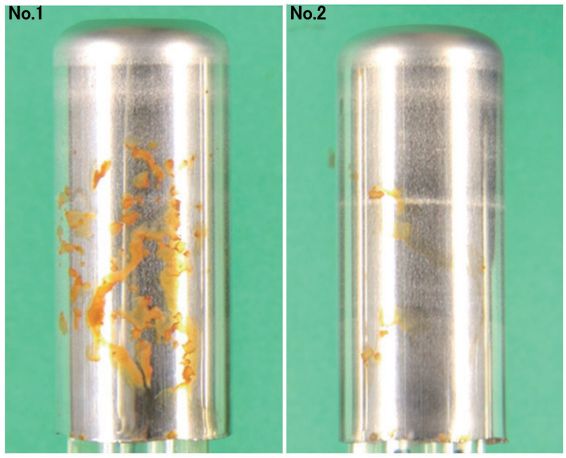

Fig. 9 Corrosion test results of Ni-coated steel cases

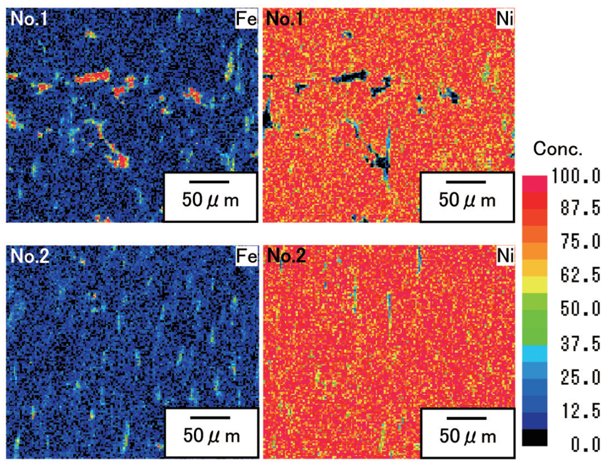

Fig. 10 Element mapping results of the outer side surface of Ni-coated steel cases

3. Result of Experiment

3.1 Structure of coating layer

Figure 7 shows the FE-SEM COMPO images of the cross sections of the coating layers. No.1 shows the image of the coating layer of which Ni-coating was applied after the annealing of the substrate material and the interface separating the Ni-coating layer a and the steel sheet b was clear. On the other hand, in No.2 of which the substrate material was annealed after coating, a new layer e was noticed on the interface. Analysis of No.3 shows that the Ni concentration is about 5mass% uniformly in the layer; the layer d exhibits graded concentration by diffusion; and only the surface layer c is a layer of pure Ni. **Table 3** shows the result of the hardness measurement of Ni-coatings before and after annealing. Ni was greatly softened by annealing. Namely, layers a and c are both pure Ni layers, however, the layer c, which has been annealed together with substrate material, is softer.

3.2 Result of evaluation of formability

Figure 8 shows the result of the observation of the cross sections of the coating layers after 1T bending. In No.1, cracks were noticed at the bent area, but they were not noticed in No.2.

Figure 9 shows the photos of the formed cases after corrosion test. As compared with No.1, No.2 exhibited remarkably low emergence of red rust.

Figure 10 shows the result of the surface analysis of the outer side surfaces of the cases by EPMA. Although the exposure of Fe was noticed in No.1, the entire surface was mostly covered by Ni in No.2, and exposure of Fe was scarcely noticed.

4. Study

Softening of the Ni-coating by annealing is considered to be attributed to the coarsening of the Ni crystal through the change from electrodeposition structure to annealed structure, as shown in Fig. 4, and to the relief of the residual tensile stress that has been accumulated in the Watt bath and exists in Ni-coating.[5)]

Improvement in corrosion resistance after forming is due to to the avoidance of the adverse effect of pinholes in one aspect as the photo shows; however, more than that, the main reason is that the Ni-coating layer was softened by annealing and the followability in forming was improved. This understanding can be obtained from the result of the bending test shown in Fig. 8, and the surface analysis of the outer side surface of the case, as shown in Fig. 10. Furthermore, it is also considered that the alloy layer formed by diffusion on the interface of the Ni-coating layer and steel sheet contributes to the improvement in the adhesive properties of the coating layer, and to the reduction of the extent of the Fe exposure.

5. Summarization

For the purpose of explaining the basic properties of SUPERNICKEL™, a sample of an ordinary Ni-coated steel sheet, No.1, and another sample simulated for SUPERNICKEL™, No.2, were prepared in the laboratory, and their properties and physical characteristics were examined.

It was made clear that SUPERNICKEL™ has a softer coating layer and greater coating adhesion than those of the conventional Ni-coated steel sheet, and therefore has excellent postforming corrosion resistance.

6. Other SUPERNICKEL™

Till date, only the excellent properties of SUPERNICKEL™ have been explained; however, the Ni-coating layer sometimes becomes prone to adhere to dyes depending on the lubricating condition in stamping since SUPERNICKEL™ has a soft Ni-coating layer on its surface layer. It is because; on a soft metal surface, a newly formed surface is prone to be exposed when the metal surface is subjected to sliding under high pressure.[6)] Adhesion of the Ni-coating layer to dyes influences the continuity of the stamping operation. As a product that does not lose its basic properties and further enhances stamping-continuity even under this kind of condition, a two-layer-type SUPERNICKEL™ wherein a hard Ni-coating is applied on the conventional SUPERNICKEL™ has also been introduced in the market as merchandize to arrange a complete product line-up.

Generally, many hard Ni-coatings contain S, and there are cases wherein the contact resistance of S-containing Ni-coating increases during storing. Battery cases made of Ni-coated steel sheets also function as a positive terminal in alkali manganese dry batteries, and as a negative terminal in Ni-metal hydride and lithium-ion batteries. In this case, the rise of the contact resistance becomes a cause of contact failure. **Figure 11** shows the contact resistance of various Ni-coated steel sheets after being stored for 10 days at 60°C under the relative humidity of 90%. The contact resistance was measured by the electric contact simulator CRS-1 of Yamasaki Seiki Co., Ltd. Although S-containing hard Ni-coating exhibited high contact resistance even under a light load, the two-layer-type SUPERNICKEL™ exhibited contact resistance equivalent to that of the conventional one-layer-type SUPERNICKEL™. As seen above, there is two-layer-type SUPERNICKEL™ that has the contact resistance equivalent to that of the conventional one-layer-type SUPERNICKEL™, and selection is therefore made according to the purpose of its use.

7. Conclusion

In addition to the properties explained so far, SUPERNICKEL™ can be endowed with the gorgeousness of mirror or matte finish depending on the method of surface finish, and different finish can also be separately provided to the front side and rear. Furthermore, Nippon Steel & Sumitomo Metal is the sole iron and steel company that provides an integrated production system from steelmaking to Ni-coating, and the properties of the substrate material can also be adjusted in any way in addition to the Ni-coating properties explained so far in this article. By taking advantage of such superiority, the authors are hereafter determined to continue to supply SUPERNICKEL™ that meets users' needs.

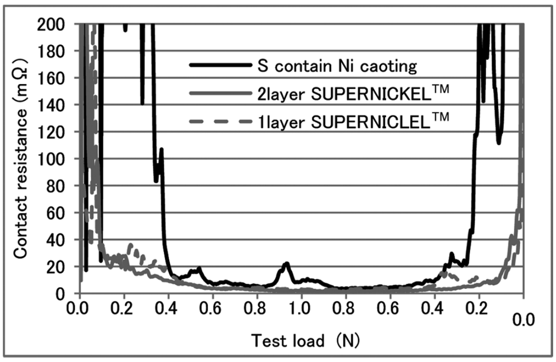

Fig. 11 Contact resistances of various Ni-coated steel sheets (after 10 days at 60˚C, 90%RH)

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Takehiro TAKAHASHI
Senior Researcher
Hirohata R&D Lab.
1 Fuji-cho, Hirohata-ku, Himeji City, Hyogo Pref. 671-1188

Kiyokazu ISHIZUKA
Senior Researcher
Hirohata R&D Lab.

Koji KAWANISHI
General Manager, Head of Dept.
Electrolytic Tinning Sheet Quality Control Dept.
Production & Technical Control Div.
Hirohata Works