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ALSHEET™ with Excellent Heat Resistance for Electrical Appliances

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Abstract

In this paper, the concept to improve the heat resistance at elevated temperature and the performance characteristic of ALSHEET™ (aluminized steels) for electric appliances is described. When the base steel contains soluble N, an AlN layer is formed between Al-Fe-Si intermetallic compound and the base steel, and it inhibits the diffusion of Al and Fe. As a result, the glossy appearance of ALSHEET™ remains after heating at 550˚C for 200 hours. Moreover, ALSHEET™ QM with a new chromate free treatment for electric appliances is developed. It has excellent corrosion resistance, heat resistance and food safety.

1. Introduction

ALSHEET™ is an aluminized steel sheet in hot-dip process, and a material that has the following properties: good appearance of aluminum, excellent corrosion resistance, and heat resistance together with strength compatible to Fe. In particular, owing to its excellent heat resistance, application as material to a car exhaust gas system has been promoted since 1980s [1] and has also been applied to thermal appliances such as heaters and gas fan heaters, particularly to their parts used at elevated temperatures.[2] Furthermore, as building material, it is used as a roof material equipped with excellent perforation resistance,[3] and in recent years, it has expanded its application to car fuel tank material [4] and hot-stamped high tensile strength car components.[5]

The melting point of Al is about 660°C which is higher than that of Zn, and the intermetallic compound layer that is formed on the interface of coating layer and steel sheet (hereinafter referred to as "alloy layer") thickens easily. Since this alloy layer is very hard and brittle, it can be the cause of peeling of aluminized layer and damage of aluminized layer in forming. For this reason, about 9% of Si is added to Al bath and Al-Si alloy coating intended for reducing alloy layer thickness is being applied. Si is said to lower the diffusion rates of Al and Fe and improve the heat resistance of ALSHEET™.[6] As ALSHEET™ is used for heat-resisting parts in household electrical appliances in many cases; study to further improve the heat resistance is underway. Furthermore, in an oven toaster and so on, the sheet is also applied to the parts which are in direct contact with foods; therefore, food safety has also to be taken into consideration. This report states the result of the study on the improvement of heat resistance of ALSHEET™ from the viewpoints of aluminized layer and surface treatment film.

2. Technology for High Temperature Colorfast ALSHEET™

2.1 Effect of steel compositions on high temperature colorfastness

When ALSHEET™ is used for parts of thermal household electrical appliances such as a toaster and a heater; often high aluminum thermal reflectivity is required. Therefore, to maintain the high thermal reflectivity even after being heat-radiated is one of the important properties that ALSHEET™ has to be equipped with. For such application, high temperature colorfast ALSHEET™ has been commercialized. In this section, its concept and properties are described. Yet, development of surface treatment film is stated in the following section, therefore in this section, surface treatment film is not discussed.

When ALSHEET™ is heated at 500°C or above, mutual diffusion between the coating layer and the steel sheet takes place, and Al-Si aluminized layer gradually changes itself to an intermetallic compound of Al-Fe-Si system (hereinafter referred to as "alloying"). ALSHEET™ after being alloyed, changes its color to dark grey or dark, and the thermal reflectivity deteriorates greatly. Accordingly, in order to maintain colorfastness at elevated temperature, suppression of alloying is necessary.

A previous study reports that steel compositions affect the temperature at which alloying of an aluminized steel sheet starts,[7] and considers that the mass of dissolved N in steel in particular is greatly influential. N dissolved in steel reacts to Al in the Al bath and forms an AlN layer on the interface of the alloy layer and the steel sheet. **Figure 1** shows the thickness of the AlN layer of aluminized steel sheets having varied mass of dissolved N, measured by a transmission

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electron microscope. AlN thickness increases as the mass of dissolved N increases, and in the steel containing dissolved N of 0.005% or more, an AlN layer of about 200 nm is formed.

Figure 2 shows the effect of AlN layer thus formed on the alloying starting temperature. In this figure, taken on the horizontal axis is the integrated intensity of N that appears as a peak on the interface of alloy layer and steel sheet in glow discharge emission spectroscopic analysis, which is supposed to represent the mass of dissolved N. Darkening temperature was determined by examining the existence of alloying after continuous heating at the subject temperature for 200 hours. This figure illustrates that as the AlN layer formed on the interface of alloy layer and steel sheet becomes thicker, the alloying-starting temperature shifts toward higher temperature side.

Accordingly, by increasing the amount of AlN formed on the interface of alloy layer and steel sheet, suppression of alloying at and below 550°C becomes possible. In addition to controlling steel compositions as a method for controlling the AlN layer thickness, annealing after aluminizing coating is also effective is also well known. Researchers have reported that annealing at 460–500°C for 60 min is effective,[8)] and considered that annealing under this condition promotes growth of AlN further. By applying these devices, the maintenance the AlN layer thickness even if mass of dissolved N in steel is lowered is possible. High-temperature colorfast ALSHEET™ which is not alloyed below or at 550°C owing to the optimized steel compositions, coating conditions and so on are manufactured.

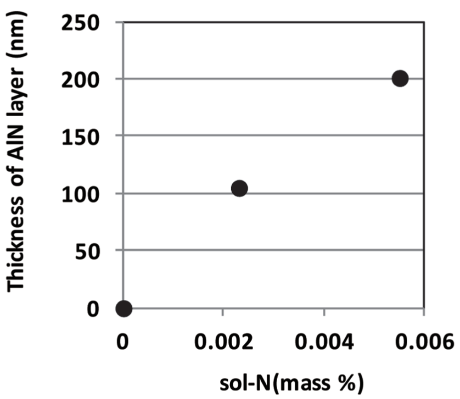

Fig. 1 Effect of solute N content in steel on the thickness of AlN layer formed between Al-Fe-Si intermetallic layer and steel

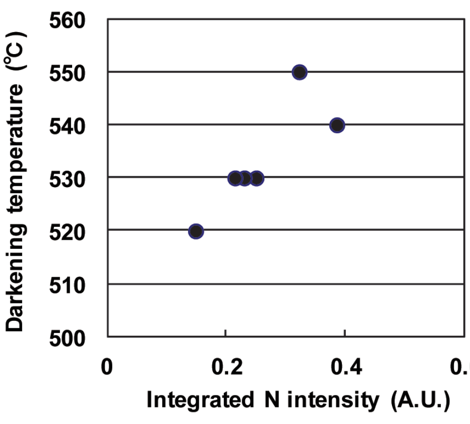

Fig. 2 Relationship between the thickness of AlN layer and darkening temperature after heating for 200 hours

2.2 Product properties of high temperature colorfast ALSHEET™

Next, concrete properties of high temperature colorfast ALSHEET™ is stated. **Table 1** shows the representative steel compositions and the mechanical properties. As stated in the previous section, to suppress alloying, dissolved N above certain mass is required. Since dissolved N degrades the material properties such as ductility and, in order to make up for such deterioration, reduction of dissolved carbon is advantageous from the viewpoint of material properties, therefore, the compositions are of ultra-low carbon system.

As for high-temperature colorfastness, darkening due to alloying does not take place even after heating at 550°C for 200 hours or at 500°C for 1 000 hours, and the sheet maintains the outlooks of aluminum. However, depending on heating condition, an interference color accompanied by the growth of oxidized aluminum film may appear. **Figure 3** shows the photos of outlooks of a conventional ALSHEET™ and a high temperature colorfast ALSHEET™, retained at 500°C for 200 hours. The conventional ALSHEET™ is alloyed and color is darkened to its surface. Contrarily, the high temperature colorfast ALSHEET™ maintains glossy outlook of Al.

Furthermore, in **Fig. 4**, photos of cross sectional micrograph of high temperature colorfast ALSHEET™ of before and after heating at 550°C for 200 hours are shown. This figure illustrates that the alloy layer thickness does not change practically even after heating at 550°C for 200 hours, and the AlN layer suppresses mutual diffusion of Al and Fe below and at 550°C. However, at the temperature of 560°C or

Table 1 Typical steel compositions (mass%) and mechanical properties of high temperature colorfast ALSHEET™

C	Si	Mn	P	N	TS (MPa)	El (%)
0.004	0.007	0.25	0.01	0.0025	332	40

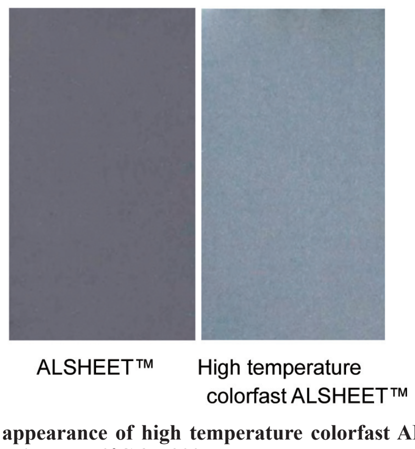

Fig. 3 Visual appearance of high temperature colorfast ALSHEET™ after heating at 550˚C for 200 hours

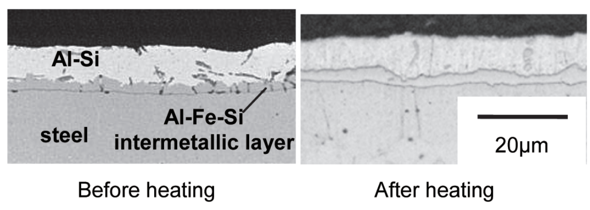

Fig. 4 Cross sectional micrograph of high temperature colorfast ALSHEET™ before and after heating at 550˚C for 200 hours

above, there are cases in which alloying is developed even for heating time shorter than 24 hours. Namely, as for suppression of Al-Fe reaction by AlN, influence of temperature is very large. AlN formed on the interface of alloy layer and steel sheet becomes unable to suppress the diffusion of Al and Fe in the temperature range at 560°C or above, of which mechanism is yet unknown in many respects.

3. Development of Chromate-free ALSHEET™ QM

Conventionally, chromate treatment was used for surface treatment of ALSHEET™. In recent years, Nippon Steel & Sumitomo Metal Corporation has developed chromate-free surface treatment for the reduction of environmental load, and has so far developed ALSHEET™ QN to be used as chromate-free ALSHEET™ as the material for car exhaust gas system and fuel tank.[9] An organic compound is added to the subject surface treatment film to improve corrosion resistance and formability and, it accompanies change in color of the film when heated. In the field of household electrical appliances, since ALSHEET™ is used for visible parts of food-cooking appliances such as an oven toaster and a bread baking toaster by taking advantage of its excellent resistance to heat, however, color change after heating becomes an issue of concern of users. Thus, it was recently decided to develop chromate-free ALSHEET™ QM excellent in corrosion resistance and colorfastness for household electrical appliances.

In order to further enhance the safety in applying to parts that are in contact with food, a study was conducted on film materials that consist of those elements and compounds which are listed and whose safety is confirmed in the list of Title 21 (hereinafter referred to as "list of compounds") of the Law of Federal Government of U.S. pertaining to food and pharmaceutical affairs (21CFR).

3.1 Concept of development

In order to secure corrosion resistance compatible to that of the conventional chromate treatment, it was decided to select alternate compounds that can perform barrier effect and inhibitor effect of the corrosion-resisting mechanism of chromate film. As requirements for the selection of alternate compounds, they had to be selected from among the elements and the compounds listed in the aforementioned list of compounds.

The barrier effect is to cut corroding factors such as water and oxygen from the corrosion reaction circuit and the inhibitor effect is to self-repair the damaged portion of the film with its own eluting film composition and to suppress the oxidization reaction of the coating film and the base steel.

In order for the film to exert its barrier effect, Oxide A and Oxide B were selected from among a number of compounds in the list as inorganic compounds that can form a film having excellent heat resistance at 300°C or above and a stabilized range of pH similar to that of the conventional chromium oxide. The water-soluble compound to be used as the material for agent to form this film was also selected from the list of compounds. The water solution of the subject compound was applied to ALSHEET™, then the sheet was dried and its film properties were investigated.

Figure 5 shows the scanning electron microscope (SEM) images of the respective film formed on ALSHEET™. As opposed to the film of Oxide A, where cracks were almost unnoticeable, a number of cracks were found on the film of Oxide B. This is due to a large difference in volumetric shrinkage and expansion in drying film.

Figure 6 shows the result of measurement of cathode polarization in 5% NaCl solution, under room temperature and under open atmosphere. Oxide A film, which does not exhibit cracks, suppresses the cathode reaction more, and furthermore, as **Fig. 7** shows, this film was excellent in terms of ratio of white rust area after salt spray testing (JIS Z 2371). Accordingly, Oxide A was selected to be the main composition of the film.

Next, as the compound for inhibitor, candidate compounds (X, Y, Z) of water-soluble inorganic compounds that exhibit inhibitor effect were selected from the list of compounds. Water solution containing 10 mass% of the candidate compound prepared for Oxide A film was applied to ALSHEET™, then, the sheet was dried. To compare the inhibitor effect of the candidate compounds at formed area, the material applied with the solution underwent Erichsen forming with the

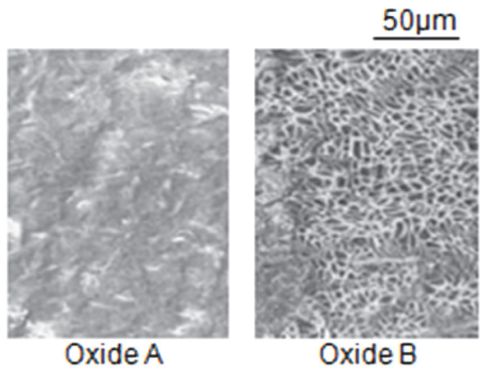

Fig. 5 Scanning electron microscope images of the oxide films on ALSHEET™

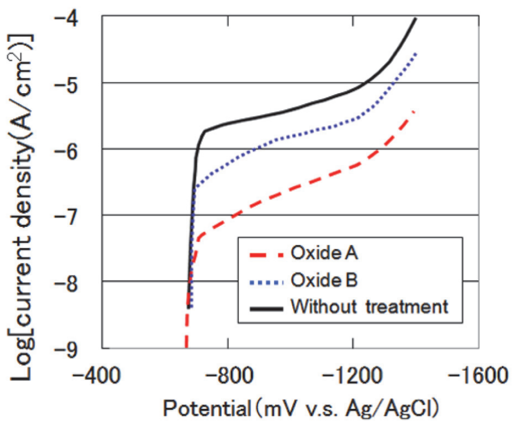

Fig. 6 Effect of oxide film on cathode polarization curve of ALSHEET™ in 5%NaCl solution

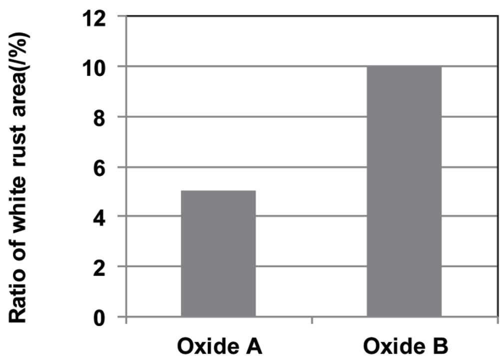

Fig. 7 Corrosion test results of ALSHEET™ with oxide film by means of salt spray 240 hours

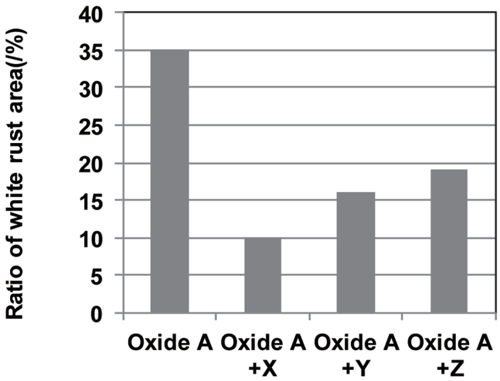

Fig. 8 Effect of inhibiter ingredient on the corrosion after forming by Erichsen

projection height of 6 mm and catered for salt spray testing. **Figure 8** shows the ratio of white rust area after 72 hours of salt spray testing. All of X, Y, and Z exhibited inhibitor effect, and from among them, X showed smallest ratio of white rust and was selected.

As mentioned above, ALSHEET™ QM was developed based on the most optimum combination of the inorganic compound film that possesses barrier effect and the inorganic compound composition that exhibits inhibiting ability. Next, the product properties of ALSHEET™ QM when used in heat-resistant parts of household electrical appliances are stated.

3.2 Product properties of ALSHEET™ QM

3.2.1 Corrosion resistance

As ALSHEET™ is used frequently in heat-resistant parts, deterioration of corrosion resistance after being exposed to heat is not preferred. On the upper side of **Fig. 9**, appearances of ALSHEET™ QM (hereinafter referred to as "QM material"), non-treated material and chromate-treated material (equivalent to 10 mg/m^2 of metallic chrome) after 72 hours of salt spraying testing are shown. Contrarily to non-treated material which exhibits color change on the entire surface, color change was almost unnoticeable on QM material likewise chromate-treated material and good corrosion resistance was exhibited. On the below side of Fig. 9, outlooks of the samples heated at 300°C for 200 hours in a furnace (open atmosphere) and after 72 hours of salt spraying testing are shown. Color change was scarcely noticed in QM material and corrosion resistance after heating was also good.

3.2.2 Heat resistance

Figure 10 shows the result of comparison of change of color (color difference ΔE^*_{ab}, as specified by JIS Z 8730) after heating at 300°C for 200 hours in a furnace (open atmosphere). The extent of color change of QM material was equivalent to those of chromate-treated material and non-treated material and good.

Table 2 shows the result of investigation on the generation of odor and smoke when heated. Stamped out samples of 44 mm in diameter were heated at 600°C on a hot plate, and the odor was checked by the sense of smell of an inspector and the smoke was visually checked by the inspector. For all of the QM material, non-treated material and chromate-treated material, odor and smoke were not perceived even after heating at a high temperature.

As stated above, ALSHEET™ QM which was designed using safety-confirmed material exhibited excellent corrosion resistance and heat resistance.

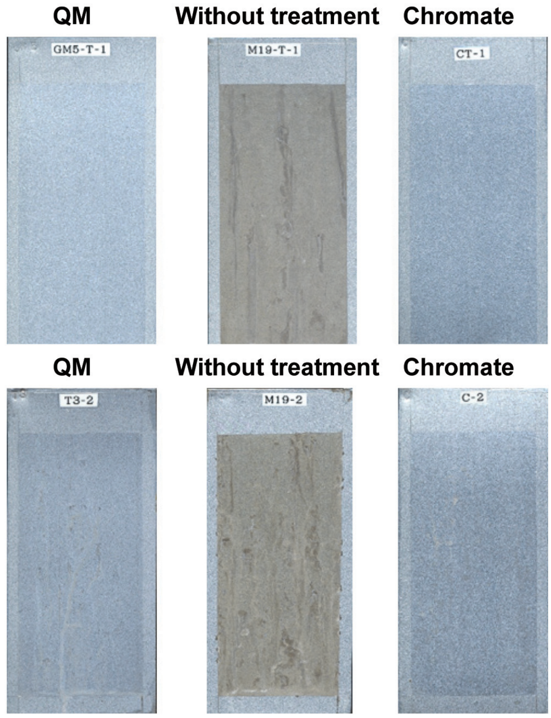

Fig. 9 Appearance of samples after 72 hour of salt spray (upper photos: as treated or plated, lower photos: heated at 300°C for 200 hours)

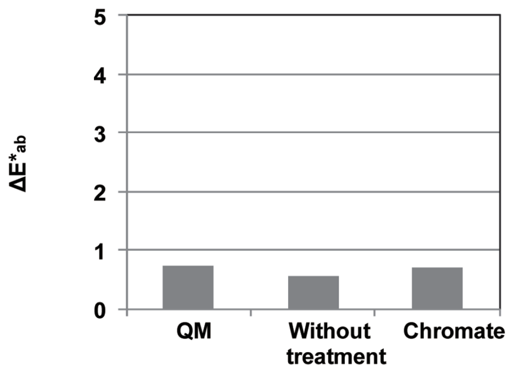

Fig. 10 Comparison of ΔE^*_{ab} after heating at 300°C for 200 hours

Table 2 Result of the reek test during heating at 600°C

	QM	Without treatment	Chromate
Smell	ND	ND	ND
Smoke	ND	ND	ND

ND: Not Detected

4. Conclusion

In this report, the concepts of the technology regarding the improvement of heat resistance and quality properties of ALSHEET™ in applying to household electrical appliances were introduced. By devising steel compositions, coating, and surface treatment film, production of ALSHEET™ having heat resistance and corrosion resistance far better than those of the conventional one has become possible. In future, further expansion of applications of ALSHEET™ in household electrical appliances can also be expected.

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