Alloying Reaction of Aluminized Steel Sheet

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Aluminized steel has excellent heat resistance because of the stable oxide film that forms on its surface. Thus, it is often used for parts that are required to be exposed to elevated temperature. When aluminized steel is heated to temperatures above 873 K, diffusion occurs between the plating layer and the steel substrate; as a result, the plating layer is composed of a mixture of several intermetallic compound layers. In this study, aluminized steel was heated at 873 K for various heating times. The composition of each layer formed on the surface of the specimens was analyzed by SEM-EDS, and each layer was identified by comparing the analyzed composition with an Al–Fe–Si phase diagram obtained by using Thermo-calc. The diffusion path between the aluminized layer and steel substrate was determined at 873 K. The layer formed in the middle of intermetallic layers was observed to have lower Al content than other layers. Judging from the composition of the layer, it can be inferred that it consists of a mixture of fine grains in two phases. TEM-EDS analysis indicated that this layer consisted of a mixture of Fe2Al5 and \( \gamma \) phase.

KEY WORDS: aluminized steel; alloying reaction; Kirkendal voids; diffusion.

1. Introduction

With excellent resistance to heat and corrosion, aluminized steel sheets, referred to hereafter as “aluminized steels”, are used as materials for various heat devices, the exhaust system of automobiles, construction materials, and so on. Stiffened and fragile intermetallic compounds which are normally called “an alloyed layer” and mainly composed of Al and Fe in the interface between the aluminized layer and a steel sheet are liable to be produced thickly, so that the deformability of aluminized steels tends to be inferior to that of galvanized steel sheets. Si addition in the plating bath is effective in restraining this growth of the alloyed layer, hence aluminized steels of so-called Type 1 with approximately 10 mass% Si added are mainly utilized in Japan. On the other hand, pure aluminized steels with no added Si are called Type 2, and produced in western continuous lines or batch type plating processes in each country as steels, used particularly when corrosion resistance is required.

Heating aluminized steels up to 873 K for a minimum of several hours promotes the growth of alloyed layers until the alloying reaction reaches to the top surface, which becomes a blackish color. It is known that when heating is extended still further, e.g. for 200 h at 973 K, diffusion advances with the surface becoming a ferrite phase having Al in solid solution.1) Since aluminized steels remaining stable against heat are frequently used at high temperatures, diverse studies regarding high temperature properties have been conducted to date.2,3,5) For instance, research enhancing oxidization resistance when using materials of an exhaust system has been conducted, revealing that adding Ti of 0.1 mass% as a minimum in steel allows us to significantly improve oxidization resistance5); implemented both domestically and abroad. Nevertheless, there are very few instances of analysis on the type of reactions that occur in the process of alloying these aluminized steels of Type 1. Ito et al.5) analyzed their sectional structure and composition after heating under various conditions to demonstrate the possible presence of 7 types of phases; however, examination as to which among them are generated specifically remains insufficient. While identification regarding compounds of Al–Fe according to X-ray diffraction has been attempted in studies by Yamada et al.,5) the only inference is that phases exist, the crystal structure of which differs in each case regarding Al–Fe–Si compounds. Recently Jenner et al.6) and Fan et al.7) investigated the intermetallic compounds formed in the alloyed layer on the aluminized steels of Type 1 heated above 1 123 K and stated that Al7Fe2Si, Al2Fe2Si, Fe2Al5, FeAl2 and so on were identified. However, the alloying process between Al–Si plating layer and the steel substrate remains obscure.

In the present study, alloying processes have been discussed by analyzing the composition of diverse phases produced when heating aluminized steels, and surmising each phase by contrasting those results against the phase diagrams.

2. Experimental Procedure
2.1. Specimens

The chemical composition of the steels which were used...
as specimens in the present study is shown in Table 1. These are based on a deep drawing grade steel, which contains ultra low carbon and Ti in order to reduce interstitial C and N extremely as TiC and TiN. An ingot with components controlled in the steel-mak- ing process was turned into a coil with a thickness of 0.8 mm by hot and cold rolling, whereupon Al–9mass%Si plating (Type 1) was applied to the surface in a continuous aluminizing line. The amount of coating on both sides was approximately 80 g/m². This value approximately corresponds to 15 μm per side when converted in terms of thickness. A photograph of the post-aluminized cross-sectional structures is shown in Fig. 1. The aluminized layers are in the hypoeutectic composition of Al–Si, and it is the Si of which phases are distributed like needles in the photograph.

2.2. Heating Condition

The samples were inserted into an electricity furnace retained at 873 K, removed after a designated time had elapsed and air-cooled. It was heated in the ambient atmosphere.

2.3. Analysis Method of Aluminized Layer Composition

Cross sectional structures were observed by a microscope after heating and cooling. Specimens were etched in a 3 vol% Nital solution prior to microscopic observation, and a Normarski differential interface microscope was used, if necessary. In order to analyze the composition of aluminized layers alloyed by heating, quantitative analysis was conducted by Energy-Dispersive X-ray Spectroscopy (EDS) attached to a Scanning Electron Microscope carrying a Field-emission Electron gun; FE-SEM S-4300SE from Hitachi Co. Ltd. In addition, the specimens were processed into fine strips using Focused Ion Beam (FIB) processing technology, which were analyzed in their still more micro regions by using a Transmission Electron Microscope carrying a Field mission Electron gun; FE-TEM HF-2000 from Hitachi Co. Ltd.

3. Experiment Results and Discussion

3.1. Alloved Status after Heating

The respective cross-sectional optical micrographs of specimens, each of which was retained for 500 h in the furnace at 873 K and for 200 h in the furnace at 973 K respectively are shown in Fig. 2. The specimen retained for 500 h at 873 K presents a doubled layer cross-sectional structure.

Conversely, that retained for 200 h at 973 K represents a single layer, and this case is assumed to be completely a ferrite phase with Al in the solid solution. The specimen retained at 973 K sees the total aluminized depth thicken, since the Al in the aluminized layer diffuses into the steel. These results are almost consistent with those studied by Ito et al. 1

Subsequently, the specimen retained for 500 h was analyzed by SEM-EDS from its section so as to confirm phases produced at 873 K. Sectional Secondary Electron (SE) images and analysis results of sectional lines are shown in Fig.
3. At the same time, spot quantitative analysis was also conducted on the respective analyzed positions represented by each number of 1–5. The images differ somewhat between the optical micrograph and the SE, and four kinds of layers were observed in the SE images from the steel sheet side. These four layers are A, B, C and D from the steel texture, and the quantitatively analyzed positions are 1 to 5 in Fig. 3.

It emerges from the results of line analysis in Fig. 3 that the distribution of Fe concentration within the alloyed layers varies continuously in layer A that are closest to the steel texture, and has a more or less consistent composition in layers B and D. However, the Fe concentration in layer C rises slightly more than that in layers B and D. The distribution of Al concentration in layer C descends as compared to that in layers B and D. Conversely, the Si concentration rises in layer C. Since there is no significant difference among the Fe concentrations, part of Al might be substituted by Si in layers B, D and C. Every concentration of Al, Si and Fe varies in layer C to indicate a specific behavior. So, we henceforth conveniently refer to this position as a low Al part.

In order to know what compounds are produced in the respective position, each quantitative analysis value in points 1–5 in Fig. 3 was plotted on an 873 K isothermal phase diagram of Al–Fe–Si. Al–Fe–Si isothermal phase diagrams were plotted through calculation by Thermo-calc5) with the thermodynamics data of this system according to Lie et al.9) Such results are shown in Fig. 4. Representative composition and crystal structures regarding the compounds (α, β, and similar) shown in Fig. 4 are listed in Table 2. Points 3 and 5 are superimposed since they have virtually the same composition, but points 1 and 3, 5 may belong to the bcc_B2 and Fe2Al5 phases respectively. Although points 2 and 4 cannot belong to any single phase, they are positioned on the respective lines joining bcc_B2 and τ1, and between τ1 and Fe2Al5. The spatial resolution of normal FE-SEM-EDS is around 1 μm diameter; hence these phases might be incorporated under micro-state. From this phase diagram, we were unable to determine why point 4 (a low Al part) with a specific variance of Al and Fe concentration is generated, followed by examining alloying processes over time.

3.2. Changes Over Time in the Alloying Process at 873 K

The generation of the low Al part described above was examined by investigating the alloying status over time, using specimens for which the period retained at 873 K was varied from 10 min to 16 h. Cross-sectional secondary electron images of specimens retained for 10 min, 1 h, 8 h, and 16 h are respectively shown in Figs. 5–8. A doubled structure is presented in every photograph, so that the composition at several points, including the respective layers, was...
The results in which the quantitative analysis values of each point shown in the secondary electron image are superimposed on Al–Fe–Si phase diagrams are shown in Figs. 5–8. Each number shown in the secondary electron image are summarized on the phase diagram. It seems to be produced since the start of alloying. On the other hand, points 5–7 in Fig. 5 are those not yet alloyed in which the Al layer remains.

Alloying reaction reaches the surface in Fig. 6 in which it has advanced further than in Fig. 5. Point 1, which was closer to the steel sheet and point 2 had compositions corresponding approximately to FeAl₁₅ and Fe₂Al₃ respectively. The nearer points 3 and 4 to the surface side have a composition on the line joining τ₁ and τ₂, and that around the middle among τ₁, τ₂₃ and τ, respectively. When contrasting Figs. 5 and 6, it is assumed that compounds having high Al compositions such as β and γ dissipate to transform into τ₂₃ or τ.

Furthermore, Selverian et al. report that a diffusion path of Fe₅Al₁–τ₁–τ₂₃–γ–β Al side occurs when immersing a steel sheet in a bath of 3 mass% Si added to 55 mass% Al–Zn plating at 883 K for 1 800 s. There are also many unclear aspects in terms of the Al–Fe–Si phase diagram and it remains unclear as to which phase τ₂₃ corresponds to in the present report, nevertheless, the part of Fe₅Al₁–τ₁–τ₂₃–γ–β is in common.

Figure 8 shows the data for 16 h on the longer side of time duration, in which the thickness of the closest layer to the steel sheet increases compared to that of Fig. 6. The composition of this point 1 is bcc-B₂. Points 2–4 coincide with Fe₅Al₁ and point 5 is still situated between τ₁ and τ₂. Points 6 and 7 are situated between τ₁ and τ₂₃ and between τ₂₃ and γ respectively. The composition of which was consistent with that predicted from the above described diffusion path (1).

The diffusion path (1) has the part of Fe₅Al₁–τ₁–γ–β in which neither compound of Fe₅Al₁ nor γ contains Si and their ratios of Fe to Al are also similar. On the other hand, τ₁ is of a compound of which the Fe concentration differs relatively slightly from said two types of compounds, but contains Si of at least 20 mass% with an Al concentration as much as 15 mass% lower. When traversing such a diffusion path, the phenomenon observed is that the Fe concentration does not change significantly, while a decrease in Al concentration and an increase in Si concentration occur in a point, which presumably corresponds to the low Al part appearing in the results of the line analysis in Fig. 3. Similarly in Figs. 5–8, it seems to correspond to this diffusion path whereby the points appearing to correspond to the low Al part were distributed mainly on the line joining Fe₅Al₁ and τ₁.

Point 2 in Fig. 4 has the compositions presented on the
line joining $\tau_1$ and bcc. While $\tau_1$ is produced in the diffusion path (1), $\tau_1$ and bcc are joined by a tie line in the phase diagram in Fig. 4, so that a transforming directly from $\tau_1$ once produced to the bcc can also exist. A diffusion path surmised from those described above is presented in Fig. 9. Despite no indication in this figure, as described above, there may be a path of $\tau_{31}$ to $\tau_{11}$, or $\tau_1$ to bcc, hence it is surmised that the form of the alloyed layer becomes complicated.

3.3. Microstructure of the Alloyed Aluminized Layer

In considerations before this section, it was surmised that the low Al part appearing in the specimen heated for 500 h at 873 K had a structure mixed microscopically with $\tau_1$ and Fe$_2$Al$_5$. TEM observation and EDS analysis were attempted to verify the validity of this assumption.

The results conducted by TEM observation after FIB processing of the section of a specimen which was heated during 500 h at 873 K are shown in Fig. 10. TEM images were divided into four layers A–D because of contrasting TEM-EDS analysis results against those results in Fig. 4. Those images allow us to confirm that the grain size of layer C have generally become finer. This layer is indicated to promote visibility by inserting lines into the corresponding layers of TEM images. This layer is supposed to represent the low Al part. Layer A closest to the steel texture and layers B and D correspond to bcc_B2, and Fe$_2$Al$_5$, respectively.

Magnified photographs of this layer with a fine grain size are also shown in Fig. 10. The grains of this layer are very microscopic with grain diameters of 0.5–1 $\mu$m. Identification of each grain was attempted from the composition of respective grains measured by EDS. Now, the reason for identification from the composition is the fact that identification from the electron beam diffraction was difficult since the crystal structure of $\tau_1$ was not yet clear as shown in Table 2. Symbols “a” and “b” are assigned to the grains, corresponding to the respective grains from which the single analysis value that Si of approximately 20 mass% was contained and the other analysis value that little Si was contained, were respectively obtained. The quantitative analysis results concerning the composition of these grains are shown on the phase diagram in Fig. 11. The composition of the grains containing Si coincides approximately with that of $\tau_1$, which allowed us to verify that the $\tau_1$ was actually produced. While it is difficult from composition alone to determine exactly which of FeAl$_2$ or Fe$_2$Al$_5$ can be attributed to grains which do not contain Si, it was surmised from the analysis results in Fig. 4 that Fe$_2$Al$_5$ was to be produced.

Based on the above analysis results, the low Al part indicating a specific distribution of Al and Si concentration values noted in Fig. 3 is surmised from the assumed diffusion path to comprise fine grains of $\tau_1$ and Fe$_2$Al$_5$. The low Al part in Fig. 3 is assumed to have been low in Al concentration and high in Si concentration, since between $\tau_1$ and Fe$_2$Al$_5$, despite no significant difference in the Fe concentration, a significant difference is obvious in the concentration of Al and Si. It is presumed from the diffusion path in Fig. 9 that many transformations were needed until producing $\tau_1$ so that the crystal grains at the low Al part became microscopic.
4. Conclusions

(1) Retaining aluminized steels during an extended period (500 h) at 873 K allows them to become alloyed to the surface so that their sectional structure is double-layered. There exists a layer (a low Al part) in which the distribution of Al, Si and Fe presents a specific behavior when element distribution of these layers is observed.

(2) This low Al part is produced from the beginning of alloying (after being retained for 10 min) and its composition lies on the line joining $\tau_1$ and Fe$_2$Al$_5$ on the ternary phase diagram of Al–Fe–Si.

(3) A TEM analysis of the low Al part allowed us to determine this point as a mixture of $\tau_1$ and Fe$_2$Al$_5$ as microscopic as 0.5–1 $\mu$m. It is assumed that generation through many transformations resulted in fine grains.

(4) The diffusion path of aluminized steels when alloying at 873 K was surmised.

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