Abridged version

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# Development of 590 MPa Grade Galvannealed Sheet Steels with Dual Phase Structure*


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## 1 Introduction

In recent years, reducing the weight of automobile bodies and securing the anti-collision property have become important tasks in the development of sheet steels for automotive applications. From the viewpoint of weight reduction, a variety of high strength automotive sheet steels with excellent press formability has been developed up to the present. Among these, tensile strength of 590 MPa or higher, combined with high ductility, can be easily obtained in dual phase sheet steel (DP steel), which has a martensite structure in the main ferrite phase. Because this material has a low yield point, these sheets are characterized by excellent shape-fixability.[1,2] Moreover, the anti-collision property has become a high priority in recent years. DP steel also provides superior performance in this regard, showing a large absorbed energy at high strain rates in comparison with other materials of the same strength.[3,4] Thus, DP steel is expected to enjoy increasing demand in the future as a material which is capable of securing safety as well as realizing weight reduction.

On the other hand, from the viewpoint of preventing rust in automobile bodies, various types of zinc and zinc alloy coated sheet steels have been developed and adopted in practical applications, and galvannealed steel sheets (GA), which provide high corrosion resistance at low cost, have now come to represent the main stream in coated steel sheets for automotive applications. However, control of the microstructure of the base steel and the addition of alloying elements to the base steel in order to obtain the desired mechanical properties give rise to various problems in the manufacture of GA.

This paper describes the metallurgical method which the authors developed to solve the problems involved in the manufacture of GA when using 590 MPa grade DP sheet steel with an excellent anti-collision property as the base material, together with the various properties of the newly developed sheets.

## 2 Technical Problems in Development and Principle of Manufacture

### 2.1 Control of DP Structure in Galvannealing Heat Cycle

One of the problems which required a solution in the development of the new sheet was securing the DP structure under the heat cycle used in manufacturing GA. **Figure 1** shows the differences in the heat cycles used in manufacturing cold rolled sheet steels and GA.

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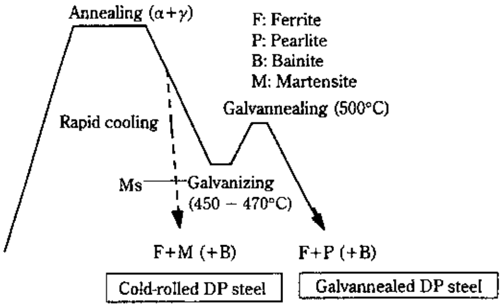



Fig. 1 Schematic illustration showing typical heat cycles of a cold-rolled dual phase steel and a galvannealed dual phase steel

In the case of cold rolled sheets, the DP structure can be obtained by rapid cooling in the annealing process from the dual phase region to immediately under the Ms point in order to obtain martensite. In contrast, the GA manufacturing process includes thermal hysteresis at higher temperatures than the Ms point. Specifically, in galvannealing, the material is immersed in a molten zinc bath in the vicinity of 460°C in a continuous process immediately following annealing, and is then subjected to the galvannealing at approximately 500°C continuously after immersion in the zinc pot. Moreover, because treatment is performed continuously in the CGL in the processes following annealing and hot-dip galvanizing, rapid cooling by water or other means is not possible in the annealing furnaces. Accordingly, in the GA manufacturing process, the average cooling rate after annealing is small in comparison with the manufacturing process for cold rolled sheets. Thus, if GA is manufactured using a base material having the same composition as cold rolled steel, it becomes difficult to obtain the DP structure, and consequently, deterioration of mechanical properties becomes a problem.

In the present development, the authors attempted to solve the problems associated with the characteristic heat cycle of GA by redesigning the alloying elements. In cold rolled DP steel, it is known, for example, that the relationship shown by the following equation exists between the critical cooling rate, CR, for obtaining the martensite structure, and the alloy content.

$$\log \mathrm{CR}\ (^\circ\mathrm{C/s}) = 3.95 - 1.73\ \mathrm{Mn\ eq.}$$

$$\mathrm{Mn\ eq.\ (mass\%)} = \mathrm{Mn} + 0.26\mathrm{Si} + 3.50\mathrm{P} + 1.30\mathrm{Cr} + 2.67\mathrm{Mo}\ (\mathrm{mass\%})$$

Cold rolled DP is manufactured using approximately 5°C/s as the critical cooling rate. In contrast to this, the average cooling rate is low with GA, at 0.5–1.0°C/s, which corresponds to Mn eq. = 2.3–2.4%. However, there is a limit to the amount of Mn addition, because excessive Mn addition deteriorates wettability with the molten zinc in the galvanizing process. This means that, in manufacturing GA, hardenability must be secured using an element other than Mn.

### 2.2 Securing Wettability during Galvanizing and Optimizing the Galvannealing Rate

It is known that elements added to steel, such as Si and others, which have a low equilibrium oxygen pressure in comparison with iron, segregate at the surface of the steel sheet due to selective oxidation of the added element during annealing, and the oxides which form on the surface are an impediment to wettability with molten zinc.[5] If wettability is poor, so-called "bare spots," which have a pin-hole shape, will appear on the surface of the galvanized sheet where the sheet has repelled the zinc, causing appearance-related quality problems. Therefore, it is not appropriate to use Si, Cr, and similar elements on galvannealed sheets as substitute elements for Mn.

Because the equilibrium oxygen pressure of P is high in comparison with that of Si, Cr, etc., it might be supposed that P addition will not have an adverse effect on wettability during galvanizing. However, it has been reported that P, which segragates on a grain boundary during annealing, impedes the diffusion of iron through the ferrite grain boundary during galvannealing, and thus sharply reduces the galvannealing rate.[6–8] Delayed alloying of GA not only reduces productivity, but also invites quality problems, such as deterioration of powdering resistance and other coating adhesion problems which result from higher alloying temperatures. In this work, the authors investigated the effect of adding Mo[2] as a substitute for excessive Mn in order to secure hardenability, and obtained excellent mechanical properties and wettability during galvanizing, as described below.

## 3 Material Properties and Galvanizing Property of Developed Steel

### 3.1 Mechanical Properties and Weldability

**Figure 2** shows the effect of the Mo content on the mechanical properties of 0.08%C-2.0%Mn steel prepared in the laboratory. As a result, it was found that steel with a low yield ratio can be obtained by Mo addition. **Table 1** shows the chemical composition of the newly developed steel; **Fig. 3** presents a comparison of the mechanical properties of the developed steel and a conventional precipitation hardened steel (HSLA steel: high-strength, low-alloy steel). By adding a small amount of Mo, on the order of 0.15%, it was possible to realize a low yield point in comparison with the conventional steel, and a high total elongation of 30%. The anti-collision property at a strain rate of $10^3\ \mathrm{s}^{-1}$ was also superior in this newly developed steel, which is a transformation hardened steel.

**Figure 4** shows the nugget diameter and button diameter in spot welding, and also shows the relationship between the welding current and cruciform tensile strength and tensile shearing strength as measures of the

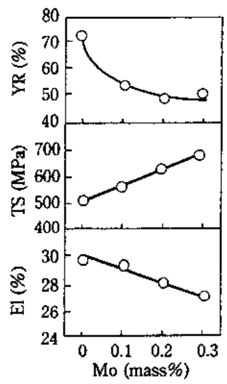



Fig. 2 Effect of Mo content on mechanical properties (without temper-rolling)

Table 1 Chemical composition of the developed steel

(mass%)

| C | Mn | P | S | Al | Mo |
|---|---|---|---|---|---|
| 0.080 | 2.00 | 0.010 | 0.005 | 0.042 | 0.15 |

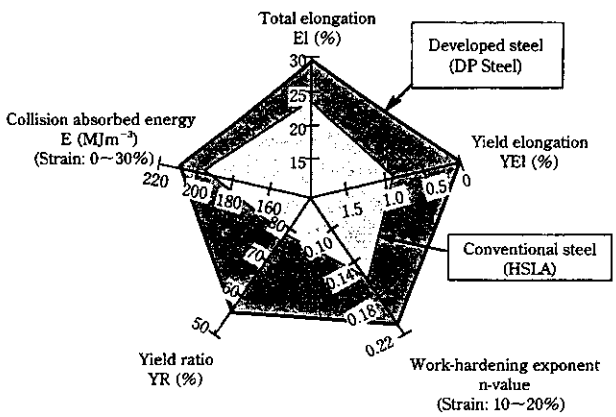



Fig. 3 Mechanical properties of the developed steel

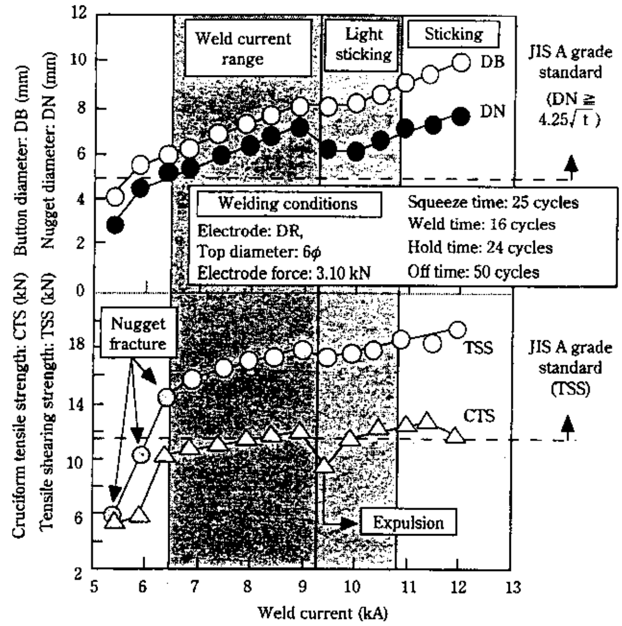
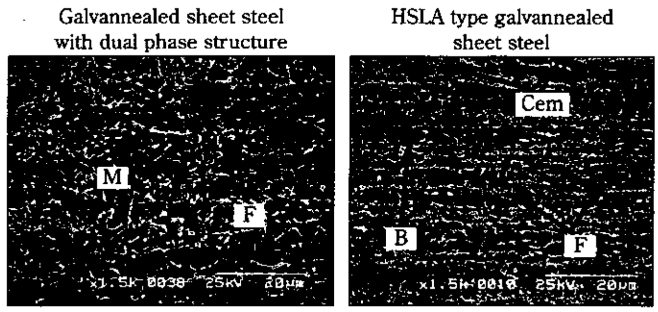



Fig. 4 Nugget diameter and tensile strength of the developed steel in spot welding (Thickness:1.4 mm)




F: Ferrite, M: Martensite, B: Bainite, Cem: Cementite

Photo 1 SEM micrographs of TS 590 MPa grade sheet steels

strength of the weld. The nugget diameter met or exceeded the JIS A class standard in the range of appropriate welding currents within which sticking does not occur, as shown in the figure. Further, the tensile shearing strength greatly exceeded the JIS A class standard in the same range of welding currents, and the cruciform tensile strength was at least 50% of the tensile shearing strength, showing satisfactory spot weldability.

**Photo 1** shows a comparison of the structures of the newly developed steel and HSLA steel. In spite of the fact that the material must be subjected to thermal hysteresis of 450–500°C in order to manufacture GA, the structure of the developed steel was that of a typical DP steel, in which the greater part of the second phase is composed of martensite.

### 3.2 Properties of Galvannealed Coating

In the GA manufacturing process, recrystallization annealing is performed in advance of galvanizing. As mentioned previously, alloying elements which are easily oxidized segregate on the surface of the steel sheet due to selective oxidation, even when the annealing process is performed in a reducing atmosphere with respect to iron, and are an obstacle to wettability with the molten zinc. Therefore, in this work, the authors investigated the surface segregation behavior of the newly developed steel during annealing.

**Figure 5** shows a comparison of the results of an investigation of the distribution of elements in the depth direction when the surface of the annealed material was sputtered by glow discharge spectroscopy, in comparison with an Si-added steel. Absolutely no segregation of Mo could be observed on the annealed surface of the developed steel, but in contrast, segregation was observed at the outermost surface of the Si-added steel. Further, the

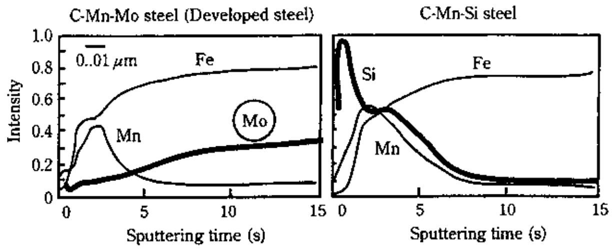



Fig. 5 GDS profiles of the annealed steel surfaces

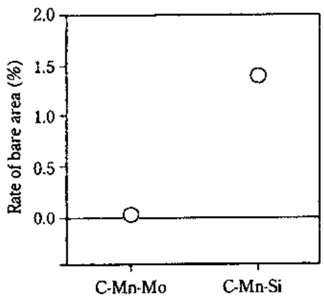



Fig. 6 Rate of bare surface area of the galvanized steels

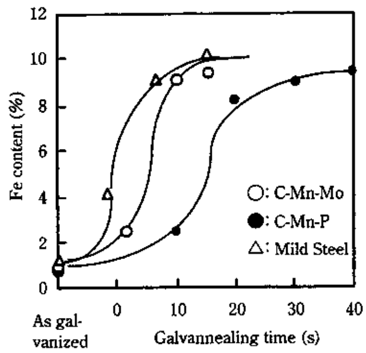



Fig. 7 Influence of substrate chemistry on Fe content of the coatings during galvannealing

rate of bare surface when hot-dip galvanizing was actually performed was measured as an index of the galvanizing property. The results are shown in **Fig. 6**. The developed steel had absolutely no bare spot, and the galvanized steel sheets had an attractive surface appearance. However, bare spots occurred on the Si-added steel.

Next, the galvannealing behavior of the developed steel was investigated in comparison with that of P-added steel, P being known generally as an element which retards the galvannealing reaction. **Figure 7** shows the relationship between the Fe content of the coating layer and the galvannealing time when a hot-dip galvanized sheet with a coating weight of 60 g/m$^2$ was galvannealed at 490°C. Galvannealing of the P-added steel was slow, and a galvannealing time of several tens of seconds was necessary in order to manufacture GA.

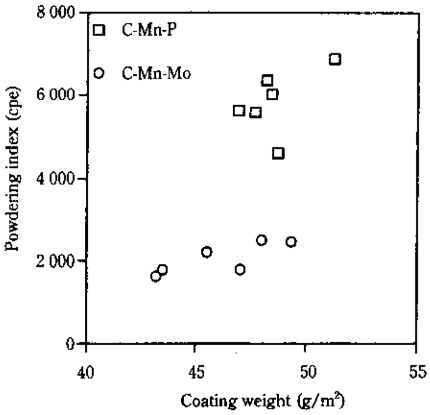



Fig. 8 Powdering resistance of the galvannealed steels

On the other hand, the galvannealing rate of the developed steel was the same order as that of mild steel, and galvannealing was completed in approximately 10 s.

When galvanized steel sheets for automotive applications are press formed, powdering, in which the galvannealed coating exfoliates in a powdery form, is considered to be a problem. The results of an investigation of the powdering resistance of the developed steel in comparison with that of P-added steel are shown in **Fig. 8**. Powdering resistance was investigated by performing a bend test with the steel sheets, and then measuring the amount of exfoliated coating which adhered to adhesive tape by the fluorescent X-ray technique. With the developed steel, the amount of exfoliation was 1/2 or less that of a comparison material with the same coating weight, showing an excellent anti-powdering property.

## 4 Discussion

### 4.1 Mechanism of Improvement of Mechanical Properties by Mo Addition

As described in Chapter 2, a larger addition of alloying elements than in conventional steels is required in order to secure adequate hardenability under the heat cycle used with GA. It was possible to obtain a typical DP structure and satisfactory mechanical properties by adding 0.15% Mo, considering the fact that excessive addition of Mn is an impediment to the galvanizing property. To investigate the reason for this , the amount of segregation of each element to the $\gamma$-phase in annealing in the dual phase region was calculated, assuming an equilibrium condition, with the thermodynamic equilibrium computation software Thermo-Calc, and CCT curves were obtained using the results (**Fig. 9**). The nose of the pearlite transformation as well as the nose of the ferrite transformation shifted to the long time side as a result of Mo addition. In other words, in Mo added steel, it is considered that re-intrusion into the nose of the

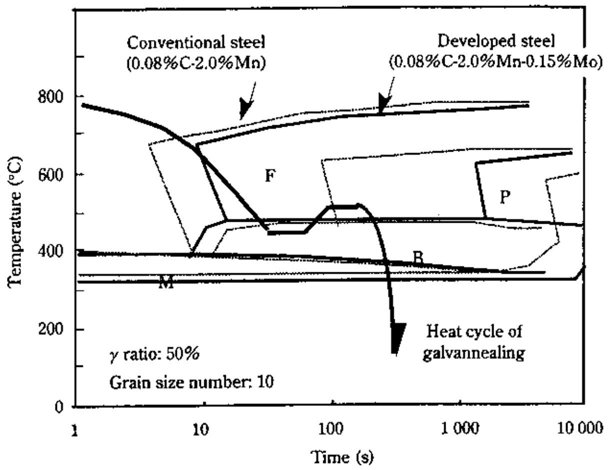



Fig. 9 CCT diagram for the developed steel and the heat cycle of hot-dip galvannealing

Table 2 Standard Gibbs free energy of formation of various oxides at 727°C[9]

| Compounds | Standard Gibbs free energy (kJ/mol) |
|---|---|
| $Cr_2O_3$ | −864.0 |
| $Mn_3O_4$ | −1 041.0 |
| $MoO_2$ | −409.4 |
| $SiO_2$ | −731.2 |

pearlite transformation during galvannealing could be avoided, and as a result, it was possible to create a stable second comprised mainly of martensite.

### 4.2 Features of Galvanizing and Galvannealing Behavior of Developed Steel

In the newly developed steel, surface segregation of Mo during annealing was not observed, and a favorable galvanizing property was secured. Similarly, from the thermodynamic data[9] shown in **Table 2**, it is considered that surface segregation did not materialize because the standard Gibbs free energy of Mo oxides is high in comparison with those of the oxides of Cr, Mn, and Si, and the amount of Mo addition to the steel was also small, at 0.15%.

From the investigation of galvannealing behavior, it was found that the galvannealing rate of the developed steel is equal to that of mild steel. The results also indicated that the alloying elements Mo and Mn do not have a retarding effect on galvannealing, such as that shown by P. For this reason, production is possible even in an actual operation without slowing the line speed in order to secure the time necessary for galvannealing, which is also an advantage from the viewpoint of productivity.

Further, it has been reported[10,11] that the anti-powdering property deteriorates at higher galvannealing temperatures. With the developed steel, it is considered that a satisfactory anti-powering property can be maintained because it is not necessary to perform galvannealing at higher temperatures than required, as galvannealing is not delayed.

## 5 Conclusion

A new 590 MPa grade galvannealed sheet steel was developed for the purposes of reducing auto body weight and improving the anti-collision property. The results are summarized below.

(1) It was possible to obtain a martensite structure, even in the GA production process, by adding 0.15% Mo to conventional DP steel in order to secure hardenability.
(2) The developed steel possesses an excellent anti-collision property, and showed 30% total elongation and a marked decrease in the yield point. Furthermore, spot weldability was good.
(3) Mo does not deteriorate wettability during hot-dip galvanizing because it does not segregate to the material surface during annealing, and it was therefore possible to obtain a coating which was free of bare spots and possessed satisfactory quality in terms of appearance.
(4) Because the P content of the steel is low, galvannealing is not delayed, and galvannealing was possible with no loss of productivity. The anti-powdering property was also of a level which presents no problems for use in the outer panels of auto bodies.

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