Note

Effect of the Steel Substrate on the Kinetics of Iron Enrichment and on the Processing Variables of Hot-dip Galvannealed Coatings on Steel Sheets

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It is normally accepted that for hot-dip galvannealed coatings best properties are obtained for a coating iron content between 10–11 mass%. In a series of works^{1–10)} both the isothermal and non-isothermal kinetics of iron enrichment of the zinc coating have been quantitatively modeled taking into account factors such as coating mass and aluminum content. That modeling was combined with the time-temperature path followed by the moving sheet during the galvannealing cycle. This time-temperature path depends on the line velocity and the galvannealing furnace. An example of a time-temperature path is given in Fig. 1 obtained by passing a sheet through a galvannealing furnace with a velocity of 1 m/s. This combination of the kinetic modeling with the time-temperature path produced the “processing windows” proposed by Lopes *et al.*¹⁰⁾

Those previous papers focused exclusively on hot-dip zinc coated sheets in which an interstitial free, IF, steel was the substrate. However it is well-known¹¹⁾ that the steel substrate has a profound effect on the subsequent kinetics of iron enrichment of the zinc coating: low carbon substrates result in a considerably slower iron enrichment kinetics when compared with IF steel substrates. This fact has in it-

Fig. 1. Temperature profile of a steel sheet in a galvannealing furnace as a function of furnace length. The sheet velocity is 1 m/s. The heating stage is 7.5 m, the soaking stage is 10 m and in the cooling stage the cooling rate is 10°C/s.

self not only a fundamental but also a significant practical importance.

In this work the effect of the steel substrate on the kinetics of iron enrichment and on the processing window of hot-dip galvannealed coatings on steel sheets is investigated.

Two hot-dip galvanized steel sheets were used. Both were produced in zinc baths with similar Al content, 0.20 mass% (nominal) and similar coating weight, 80 g/m² (nominal). On one sheet the substrate was a Ti-IF steel and on the other a low carbon steel. The substrate chemical analysis were (in mass%): C - 0.0035; Mn - 0.14; P - 0.01; S - 0.007; Si - 0.006; Ti - 0.07; N - 0.003; Al - 0.05; Fe - balance and C - 0.04; Mn - 0.15; P - 0.01; S - 0.01; Si - 0.003; N - 0.004; Al - 0.04; Fe - balance, respectively. Specimens measuring 100×100×0.85 mm were taken from the same side of each sheet and annealed in salt bath at 450, 475, 500, 525 and 550°C for holding times ranging from 5–120 s and water quenched (cooling rate about 90°C/s). The heating rate was about 40°C/s and the annealing times were measured from the instant the specimen reached the required temperature. From the center of the specimens disks with 60 mm in diameter were taken for the determination of iron content. This was done separately on each side of the disk using a sulfuric acid solution to dissolve the coating.

Figure 2 shows a comparison between the isothermal kinetics of iron enrichment of the IF and low carbon steel zinc coated sheets. The data are plotted as a time, temperature, transformation, TTT, curve. The time necessary to reach a coating iron content of 11 mass% at a given temperature is plotted. The difference in kinetics is quite substantial: the kinetics of the iron enrichment of the low carbon sheet was much slower than that of the IF sheet. It is worthy of note that in the low carbon steel sheet at 450°C after 120 s the coating iron content was still about 5 mass% and of course is not represented in Fig. 2. Another interesting point is that for the IF sheet one finds a decrease in transformation time as the transformation temperature is increased. On the other hand the low carbon sheet behavior is

Fig. 2. Comparison of the kinetics of iron enrichment for low carbon and IF steel sheets coated in a zinc bath with 0.20 mass% Al and with a coating mass of 80 g/m². The TTT curves represent the time necessary for the coating iron content to reach 11 mass% during isothermal annealing in a salt bath at a given temperature. The kinetics of iron enrichment is considerably faster for the Zn coated IF steel sheet than the Zn coated low carbon steel sheet.

different. The transformation curve has a “C” shape below 530°C. That is, the kinetics initially increases with increasing temperature then slows down as 530°C and then again increases. This latter result is virtually identical to the result obtained by Smith and Batz in an early work¹²⁾ on the iron enrichment of a low carbon steel sheet. The explanation for this is that at 530°C there is a peritectic transformation¹²⁾ above which zeta phase cannot form. So, up to 530°C, zeta phase nucleates and grows into the liquid Zn. Only after some zeta phase has formed delta phase starts to form at the substrate/zeta phase interface. Closer to 530°C, nucleation and growth of zeta phase becomes thermodynamically more difficult so that the overall kinetics is delayed. Above 530°C delta phase can form directly without previous zeta phase formation and the reaction rate increases as temperature increases. A similar effect probably also occurs in the IF sheet but the “C” shape is not evident. Perhaps due to the faster kinetics the delay in the overall kinetics might occur only very close to 530°C.

Figure 2 shows that the kinetics of iron enrichment is a function of the substrate. This will result in a different behavior of each steel during the galvannealing treatment. It is however by no means clear how exactly this will happen and whether the “C” shape of the low carbon steel coated sheet will have a significant effect. In this regard it is helpful to construct the processing windows for these steels. One can follow the same methodology used by Lopes *et al.*¹⁰⁾ that is repeated below in condensed form for convenience:

1—First, the isothermal iron enrichment kinetics of the IF and low carbon steel sheets are obtained. This was done by isothermal annealing of the samples within the temperature interval of 450–550°C for times ranging from 0–120 s and analyzing the resulting iron content in each case.

2—The data obtained in step 1 are fitted by a simple isothermal model^{1,2)}:

$$W = W_0 + (W_s - W_0) (1 - \exp(-kt)) \dots \dots \dots (1)$$

where W is the coating iron content, W_s is a saturation coating iron content and W_0 is the initial coating iron content, all in mass%. From such a fitting k and W_s are obtained and their values are given in **Table 1**. More details can be found in Lopes *et al.*¹⁰⁾ It is worth mentioning that this model has been used successfully to describe the kinetics of the iron enrichment on previous works^{1–6,8,10)} but it is a phenomenological model. It does not explicitly take into account the nucleation/growth mechanism of the individual phases.

3—The third step consists in defining at least approximately the temperature vs. time cycle undergone by the galvanized sheet within the galvannealing furnace. The furnace used here had three stages: a) Low frequency inductive heating stage, 7.5 m in length, in which the sheet temperature increases approximately linearly with furnace length; b) A soaking stage in which the temperature is maintained constant, a soaking stages of 10 m in length was used; c) A cooling stage with a cooling rate of 10°C/s that corresponds to forced air cooling. It is assumed that galvannealing starts at 450°C and ends also at 450°C. The profile shown in Fig. 1, as said above, is obtained by passing a sheet through a furnace with a velocity of 1 m/s. This furnace does not represent a specific furnace of any plant but

Table 1. Summary of parameters k and W_s obtained by fitting Eq. 1 to data acquired by isothermally annealing hot-dip galvanized steel sheets. W_0 (mass%) was taken as zero on both steels.

0.20 mass% Al bath coating on low carbon steel substrate (80 g/m ²)		
T (°C)	k (s ⁻¹)	W _s (mass%)
450	0.0373	4.8
475	0.0192	12.8
500	0.0179	14.6
525	0.0166	13.1
550	0.122	13.5
0.20 mass% Al bath coating on IF steel substrate (80 g/m ²)		
T (°C)	k (s ⁻¹)	W _s (mass%)
450	0.0191	14.2
475	0.0351	13.5
500	0.108	12.7
525	0.159	13.2
550	0.0901	14.4

Fig. 3. Comparison of the processing windows for low carbon and IF steel sheets coated in a zinc bath with 0.20 mass% Al and with a coating mass of 80 g/m² galvanneal with the furnace profile showed in Fig. 1.

is thought to be representative of a possible galvannealing furnace.

4—In the fourth step one uses $k(T)$ and $W(T)$ obtained in the second step together with the temperature profile defined in step 3 to calculate the coating iron content after the annealing treatment. In order to do this one can use one of the two methods suggested by Seixas and Rios^{1,6)}: additivity and integration of the kinetic law. In this work the direct integration of the kinetic law was chosen as it was easier than the additivity method used by Lopes *et al.*¹⁰⁾. The differential equation that represents the kinetic law¹⁾ was directly integrated for a non-isothermal cycle, $T(t)$:

$$\frac{dW}{dt} = k(T(t))(W_s(T(t)) - W), \quad W(0) = 0$$

5—Finally one can plot the calculated results as the “processing window” shown in **Fig. 3**. In order to construct such a processing window one plots the soaking stage tem-

perature on the vertical axis and the line velocity on the horizontal axis. One then chooses a given soaking temperature say 500°C and calculates the line velocity that will result in a coating weight of 11 mass% Fe. This will be the minimum line velocity since line velocities lower than this will result in coating iron contents higher than 11 mass% Fe. One also calculates the line velocity that will result in a coating weight of 10 mass% Fe. This will be the maximum line velocity since line velocities higher than this will result in coating iron contents lower than 10 mass% Fe. As one repeats this calculation for several soaking temperatures two lines are generated. Within these two lines is the “processing window” and within it any combination of line velocity and soaking temperature will produce a coating iron content within the desired limits of 10–11 mass% Fe.

Figure 3 shows the processing window for the IF and for the low carbon steel sheet. As expected they are very different. It is worthy of note that the shape of the processing window for the low carbon steel between 475 and 525°C parallels the shape of the TTT curve of the low carbon steel shown in Fig. 2. This is reasonable as the processing window was calculated from the same isothermal kinetics data as the TTT curve. As explained above, the reason behind this somewhat unexpected result is probably that, although one expects the diffusion rate to increase with temperature, the formation of the zeta phase becomes thermodynamically more difficult as the temperature is increased from 475 to 525°C since the zeta phase is not stable above 530°C. As a consequence, the overall reaction rate does not increase but has a typical “C” shape. The shape of the processing window of the low carbon steel reflects this fact. One can see in Fig. 3 that the lower carbon steel sheet requires much lower line velocities than the IF steel to reach the desired 10–11 mass% Fe content due of course to its slower kinetics. The line velocity required to reach the desired 10–11 mass% Fe content would be too low, about 0.2 m/s, for practical purposes. Another interesting point is that to increase the soaking temperature is of little help. Only for temperatures above 525°C the reaction starts to become faster. A reasonable line velocity of 1 m/s would require a soaking temperature of 550°C, which is too high for practical purposes. Of course the way to go is well-known: one is forced to decrease the zinc bath Al content in order to obtain a faster kinetics at reasonable soaking temperatures and line velocities.

As shown in Fig. 3 the IF steel sheet transforms consid-

erably faster and the kinetics increases with temperature. Although in practice one uses zinc bath Al contents in the range 0.13–0.15 mass% Al from a kinetic point of view it is not unfeasible to use higher Al contents for the IF steel sheet. One can see that even for the high Al content used here, 0.20 mass% Al, it is still possible to obtain galvanized coatings for a line velocity of 1 m/s at 500°C, which are reasonable values.

It is worthy of note how isothermal kinetic data obtained in a salt bath together with an approximate galvanneal temperature cycle and simple mathematical modeling can yield results that are consistent with practical experience from the actual galvannealing process.

In conclusion one can say that the kinetics of iron enrichment of a low carbon steel zinc coated sheet is considerably slower than that the kinetics of iron enrichment of an IF steel zinc coated sheet. The implications of this fundamental effect to practical applications could be better understood with the help of the processing windows presented here.

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