Report on HS1587

Real time analysis of the very initial stages (t<10s) of the galvanization process in Al containing Zn baths : mechanism of formation of the inhibiting Fe_2Al_5 layer

Participation to the experiment

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Aim of HS1587

The goal of HS1587 was to measure the very initial stages of galvanization in Al containing Zn baths. This industrial process (hot dip galvanization) is used to produce the main part of the galvanized products for the car industry. In order to respect the requirements imposed by this industry (aspect quality and mechanical properties of the coating), Al is added to the Zn bath (at a very low concentration < 0.2 wt%). In such conditions, it has been shown that an Fe_2Al_5 layer forms first (in a few seconds) at the Fe (solid) / Zn (liquid) interface. This layer prevents the formation of FeZn intermetallic compounds which have a damageable effect on the quality of the coating [1] [2]. However depending on the experimental conditions (time, temperature, steel quality) the Fe_2Al_5 layer cease to play its inhibiting role and FeZn outburts form. The mechanisms of this inhibition breakdown are not yet clearly understood despite several analysis. One of the main reasons is that, given the very high rate of formation (or degradation) of the Fe_2Al_5 layer, the whole process takes place in some seconds at 450°C. In these conditions, any kind of post mortem analysis is subject to caution. Thanks to the high brilliance of synchrotron radiation combined with the high speed acquisition device (Frelon), ID11 offers unique possibilities to monitor this process by a real time *in situ* analysis.

Experimental approach

One difficulty of the experiment was to reproduce the industrial conditions. During HS 1587 this problem was tackled using the following set of complementary samples

"1" - Steel sheets (Interstitial Free Titanium doped steel : IF-Ti) covered with a Zn-Al (0,2wt%) coating. The coating was deposited by RF sputtering, its composition was that used in the industrial galvanization process. With these samples we expected to follow the growth of the Fe_2Al_5 layer as well as its degradation (formation of FeZn phases).

"2" - Industrial samples issued from a production line in such conditions that an Fe_2Al_5 layer (<0.1 μm) is formed in contact with steel and covered with Zn (10 μm). No FeZn phases are initially present. With these samples we were expecting to follow the degradation of the Fe_2Al_5 layer and the growth of FeZn phases.

"3" –Fe/Al multilayers deposited, by e-beam evaporation, on an inert substrate (SiO_2). This set of samples was expected to provide the kinetic of growth of the Fe_2Al_5 layer by Fe/Al solid state reaction.

"4" - Steel plates (IF-Ti) in which two reservoirs connected by a "channel" were machined (see fig. 1). One reservoir was filled with solid Zn. By tilting the whole sample at $T>T_m$ (Zn), a direct reaction between liquid Zn and steel in the channel was expected.

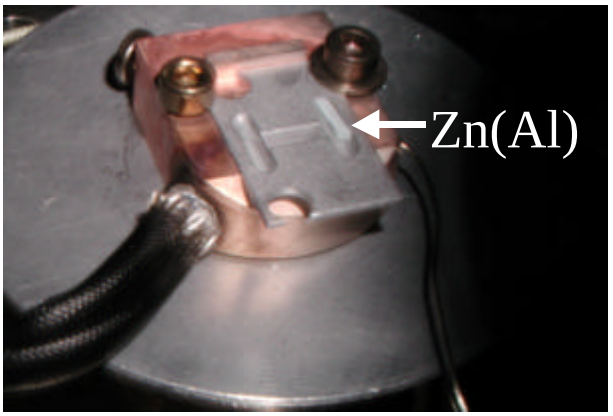

Figure 1 : I.F.-Ti machined sample (type "4")

Results

Several types of experimental limitations were encountered:

A - the vacuum chamber had to be adapted to the specific diffraction geometry, the gas introduction line had to be modified and after some filling operations the (N_2-H_2) gas bottle started to leak. Because of these difficulties only a few experiments were performed in vacuum or (N_2-H_2) atmosphere

B – The chemical quality of the Zn deposits obtained by sputtering (samples "1") was not satisfying and prevented good interfacial reaction.

C – It was impossible to obtain with samples "4", a correct reaction in the channel since in the temperature range accessible, liquid Zn did not flow from the reservoir into the channel (probably because of reactive wetting between Zn and Steel). Moreover the necessity to tilt the sample put limitation on the reproducibility of the diffraction conditions.

From these observations it appeared that a more specific experimental set up had to be defined.

Despite these limitations quite satisfying and original results were obtained with samples "2" and "3"

<u>Analysis of the inhibition breakdown and growth of Fe-Zn phases (samples "2")</u>

The following heat treatments were performed:

- 2 temperature ramps (50-470°C) with an acquisition time of 1 image/sec and 4 image/sec. In that last case only the temperature interval 415-445°C was monitored.

-7 isothermal treatments (390<T<430°C) centered around the Zn melting temperature (418°C)

Figure 2 gives a typical 3D (Temperature, time, 2θ) representation of these experiments. The different diffraction peaks can be attributed to Zn, and two FeZn phases (delta and dzeta). No diffraction line characteristic of Fe_2Al_5 were observed. This is very likely due to the fact that this layer presents a texture, and that in the chosen geometry, these planes are not in diffraction conditions.

For all experiments we observed a melting of Zn, followed by the growth of delta and dzeta. No other FeZn phase (e.g. gamma) were observed.

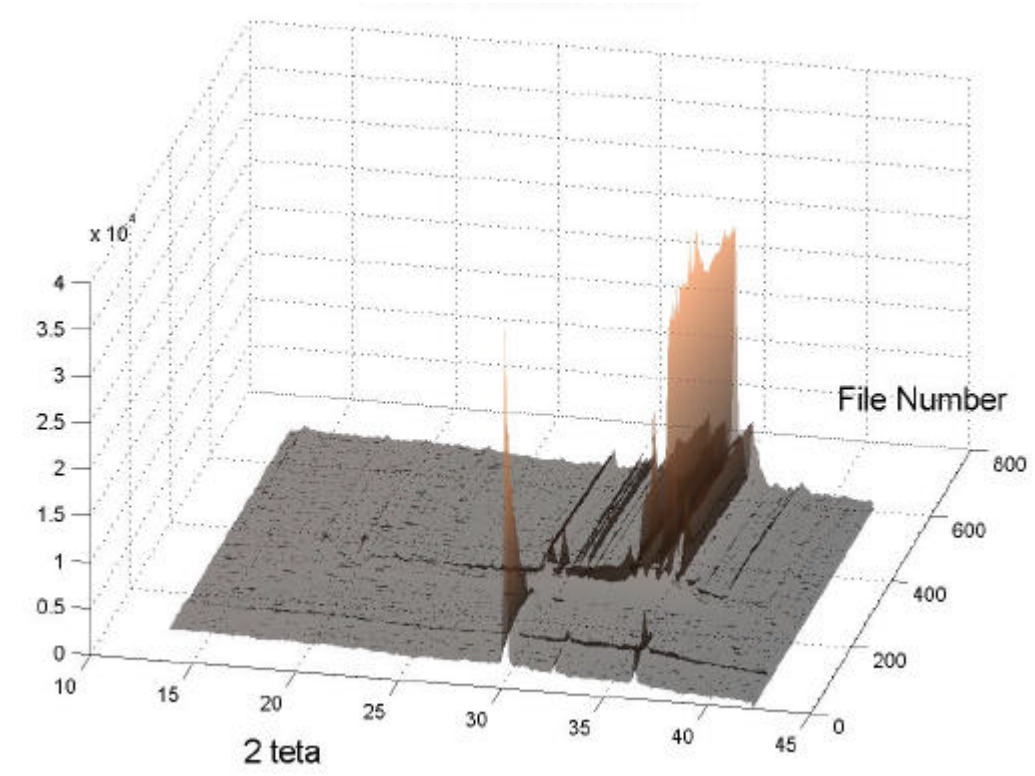

Figure 2 : 3D plot showing the growth of delta and dzeta at the Zn(Al)/Steel interface

From the intensity of characteristic peaks of delta and dzeta we could show that these two phases grow simultaneously. By assuming a planar growth we could model the growth kinetic and show that it is apparently linear with time for both phases (which thus grow according to an interface controlled mechanism [3]). The growth of dzeta is faster than that of delta (see fig.3) so that both phases grow together until total consumption of Zn, then delta grow by consuming dzeta.

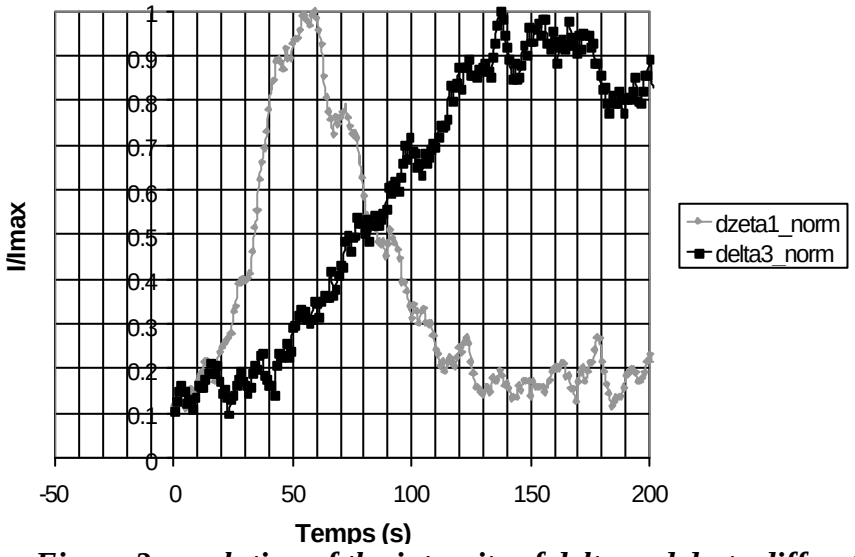

Figure 3 : evolution of the intensity of delta and dzeta diffraction peaks during a 430°C isothermal heat treatment

This behavior is similar (except the growth rate which is temperature dependant) for reaction with liquid or solid Zn (i.e. for isothermal treatments at $T<T_m$ or $T>T_m$) which indicates that the inhibition breakdown is not specifically linked to liquid Zn. (e.g. liquid Zn penetration of the Fe_2Al_5 layer). Moreover, calculations of the growth rates of delta and dzeta show that

there is no discontinuity at the Zn melting temperature. The activation energies for dzeta and delta growth are apparently very high (of the order of 5 eV for dzeta).
Right now the different samples are under microstructural analysis to confirm the absence of delta phases and to have a better idea of the growth morphology. In the present state of this study the main conclusions are:

- dzeta and delta are the first phases to appear after the inhibition breakdown,
- their growth is simultaneous and "interface" controlled,
- the same behavior is observed when steel reacts with liquid or solid Zn
- the activation energies for the growth of dzeta and delta are apparently very high.

Analysis of the growth of Fe_2Al_5 by Fe/Al solid state reaction (samples "3")

The Al/Fe multilayers chosen for this experiment had a period of 50nm, a total thickness of 300nm and a global composition (fixed by the Al/Fe thickness ratio) corresponding to Fe_2Al_5. One experiment was also carried out with an Al/Fe bilayer (same global thickness and composition).
The observations (isothermal ramp at 20°/min) showed that $Fe_2Al_5$was the first phase to form at the Fe/Al interface in agreement with several reports on Fe/Al thin film reaction. However we showed that this formation is decomposed in two steps (fig. 4)

a- preferential growth of the 110 planes until total consumption of Al and Fe,
b- restructuration of the Fe_2Al_5 layer at constant thickness.

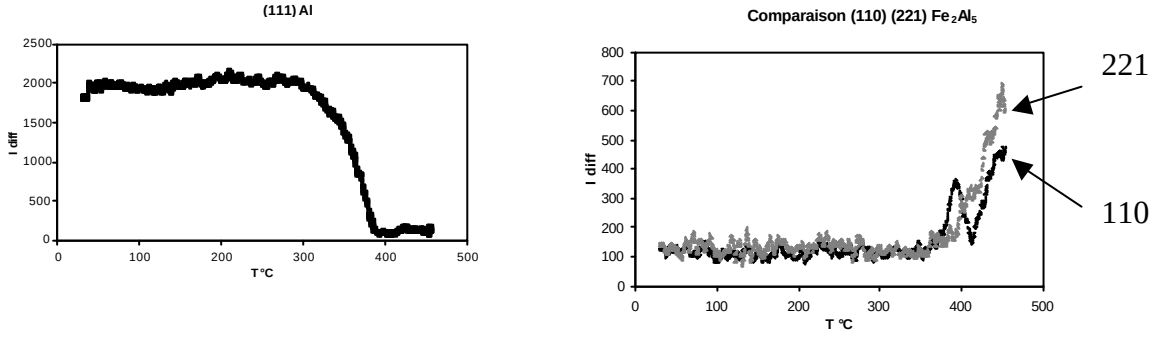

Figure 4 : evolution of the intensity of the Al and Fe_2Al_5 diffraction peaks

Using a layer by layer growth model we could show that this formation is interface controlled (linear time dependence) with an activation energy of 1.3 eV. These results agree with that obtained by differential scanning calorimetry on the same samples.
A quite interesting and original result is the preferential growth along the 110 direction. This direction is different from that observed during the growth of Fe_2Al_5 in bulk diffusion couples (001) as well as during galvanization (also (001)). In the case of bulk diffusion couples, that preferential orientation was explained by a diffusion anisotropy while in the case of galvanization it was linked to an epitaxial relation with the substrate (steel). More likely, this last explanation is also valid for the present set of experiments except that the epitaxial relation involves Al grains (the Fe film is nanocrystalline). To confirm this interpretation, analysis of the "as deposited" multilayer texture are in progress.

As a conclusion, HS1587 provided quite original results concerning:

- the inhibition breakdown and the growth of FeZn phases : nature of phase formed, kinetics of formation and growth mechanisms,

- the kinetics of growth of Fe_2Al_5 by Al/Fe solid state reaction.

These new kinetics information will allow after completion of the above mentioned additional experiments, a much better interpretation of the initial stages of Fe/Zn(Al) reactions taking place during the galvanization or galvannealing process.

Moreover, the expertise accumulated by our team during HS1587, as well as the nature of the experimental difficulties encountered will allow us to propose a more relevant experimental set allowing the direct analysis of the kinetic of formation of the Fe_2Al_5 inhibiting layer in the very first stages of the reaction between steel and liquid Zn(Al).

[1] A.R. MARDER, "The metallurgy of zinc-coated steel", Progress in materials science, 45, pp. 191 – 271, 2000

[2] M. GUTTMANN, "Diffusive phases transformations in Hot Dip Galvanizing", Materials Science Forum, vol. 155-156, pp. 527, 1994

[3] F.M. D'HEURLE, P. GAS, J. PHILIBERT, O. THOMAS, "Considerations regarding reactive diffusion : Parabolic and linear rates", Metals Materials and Processes, vol. 11, pp. 217, 1999