Centre for Research in Metallurgy

Avenue du Bois St Jean, 21
Domaine Universitaire du Sart-Tilman (P59)
BE - 4000 LIEGE
Phone : +32 4 254.62.11
Fax : +32 4 254.62.62

15/02/2017

CONFIDENTIAL

ZCO-75: "Nature of Galvanizing Wettability on Advanced High Strength Steels"

Research proposal

Galvanized Autobody Partnership (GAP)

Available Project Budget & Project Duration: $60,000 per year for a 3-Year Period

Research Leader: D. Debrabandere
Project Associate: L. Bordignon

ZCO-75: "Nature of Galvanizing Wettability on Advanced High Strength Steels"

1. Project Objective and Scope:

The objective of this program is to explore the limits of wettability of advanced high strength steels, primarily focusing on steels that have been prepared using an oxidation-reduction treatment prior to hot dipping, with significant attention paid to the nature of the substrate surface at the point of hot dipping. The study will be limited to selected dual-phase steels, together with a control composition of a simple IF steel. Compositions will be chosen that have a range of Mn, Si, Al, Cr and other industrially important alloy compositions; sponsors have indicated that high-ductility Si-containing DP grades are of high interest. These would then be subjected to relevant galvanizing process pretreatment steps, including process routes incorporating reduction only, external selective oxidation only, and oxidation-reduction treatments selected by sponsors. These surfaces would be well characterized before contact with the liquid Zn coating alloy. The nature of wettability can then be studied in several ways, including wetting angle, microstructure examination of wetted versus non-wetted areas, the nature of the coating/steel interface after galvanizing for various periods of time and coating composition and microstructure features near the interface. Characterization of coating adherence after cooling would also be useful to check and relate to the wettability results. A key question to be answered is how the limits to Zn alloy coating wettability are determined by the details of oxide structure on and near the substrate surface. This is expected to include an examination of detailed morphologies of surface oxide particles (granular, film-like and other morphologies), the area fraction of coverage of oxides on the surface of the substrate, oxide compositions, thickness and roughness and other details relevant to wettability. If possible, the physical limits to zinc wettability, in terms of oxide particle size, spacing, height and other details will be determined that will be of great value in galvanizing process design for existing steels and new compositions to be developed. Of great practical importance is the flow condition of the liquid Zn that participates in the wetting reaction. Oxides that are either contained in the liquid metal, or form and then grow for a time more than a few seconds as a result of the wetting of the substrate, can interfere with wettability and, more importantly, would not typically be found in the continuous galvanizing process we are modelling. The influence of fluid flow on wettability, for velocities expected in continuous lines, should be included in the scope of this project.

2. Proposed research program

2.1. Steel composition

Two steel grades will be selected for the whole program. 10 m² of each of these steels have to be delivered by sponsors and has to contain at least 1.5%Mn + 1.5% (Al+Si) and eventually additional alloying elements like Cr and B. An annealing cycle has to be also proposed for each steel grade, so that optimum mechanical properties can be associated with good coating performance.

As requested, an IF Ti will be used as a reference for the whole program. However, the real question is: how to transpose the wetting angle, measured by the sessile drop method, to the

zinc reactivity in industrial configuration? Indeed, wetting improvement will be observed with an adapted atmosphere composition, but will it be sufficient to guarantee a good galvanisability on industrial lines? Therefore, a DP500 should also be added as a reference because this alloyed steel grade, which should contain around 1%Mn+0.4%(Si+Cr), can be correctly galvanized in all lines without adaptation of the atmosphere composition. Consequently, for being acceptable for industrial application, all the modified atmosphere conditions should allow obtaining zinc wetting angles at least lower than the one measured for a DP500 while being as close as possible to the IF Ti measurements after a standard annealing (800°C/ 60s / 5%H_2 / DP-30°C). In a general manner, previous trials have shown that after 3 seconds of contact of a zinc droplet with these 2 steel grades, the wetting angle is respectively 47° for an IF Ti steel and 92° for a DP500 (Figure 1). Therefore, the zinc wetting angle should be between 45° and 90° to guarantee good zinc reactivity.
Concerning the reference steel grades (IF-Ti-DP500), 2m² will be sufficient to simulate the standard galvanizing conditions

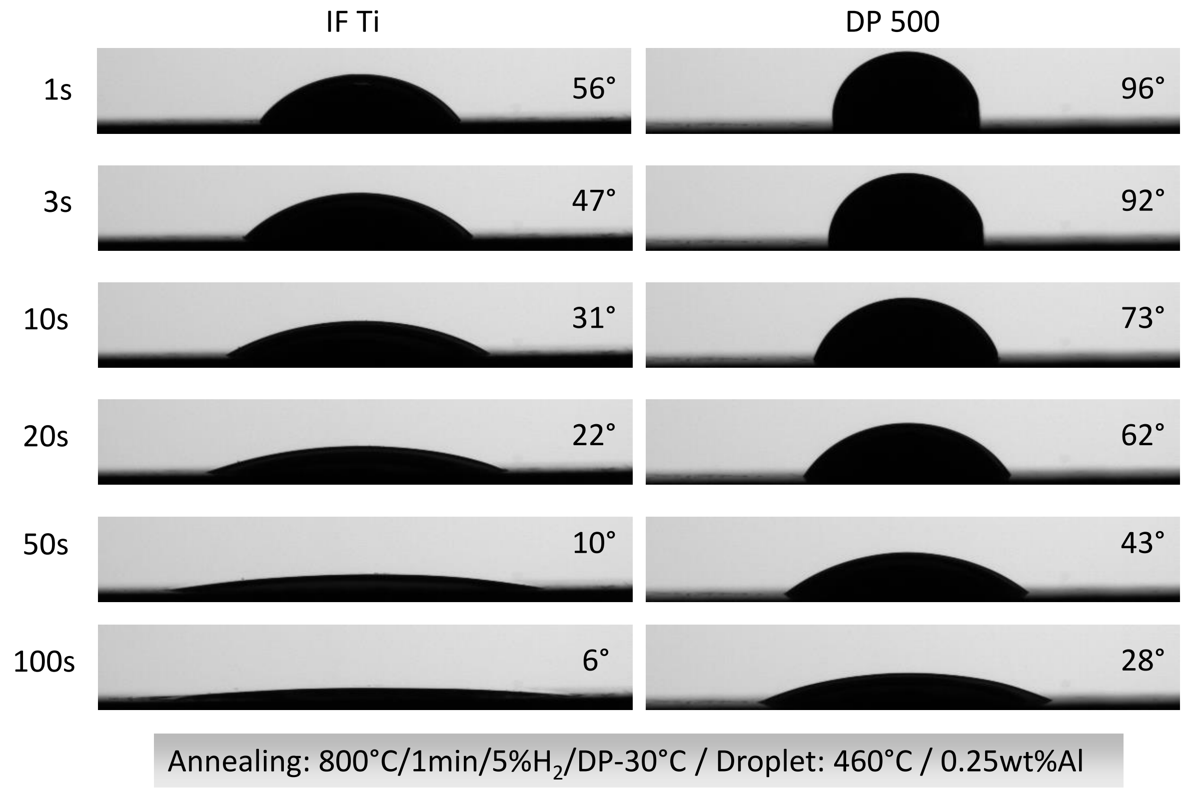

Figure 1: After 3s of contact, the wetting angle of the zinc droplet should be in range between 45° and 90° to guarantee a sufficient reactivity during dipping.

2.2. Proposed program

The proposed program is schematically summarized in Figure 2. It is intended to:

- Study the influence of an oxidation/reduction process or an internal oxidation in comparison with a classical annealing condition.
- Determine their influence on zinc wetting and coating adhesion.

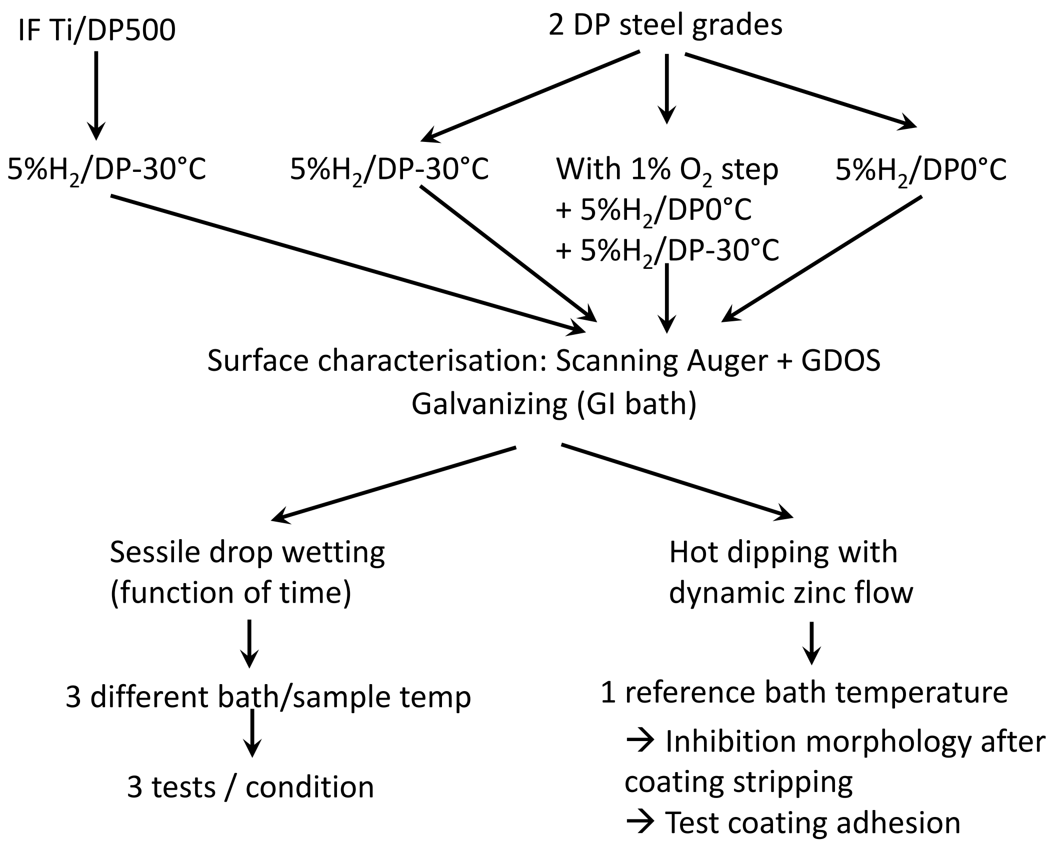

Figure 2: Schematic program proposed

2.2.1 Multidip experiments

A single simulator (Figure 3) will be used to study the different annealing in oxidizing and reducing conditions as well as the dipping with a zinc flow, without any interruption in the thermal cycle.

More precisely, the study of the annealing conditions has to be made in 3 steps:

- Make surface analyses before and after the oxidation step, which has to be made between 0.5%O_2 and 2%O_2 at 650°C during 3 seconds. Indeed, according to our experience, an atmosphere containing 1%O_2 should be selected to obtain an iron oxide thickness of ± 200 nm. The iron oxide growth however depends on the surface preparation before entering in the oxidizing section. Indeed, the presence of a too continuous external selective oxidation before the iron oxide step could decrease the oxidation rate. Therefore, it is foreseen to make the heating step in external (5%H_2/DP-30°C) or internal (5%H_2/DP0°C) oxidation conditions. This oxidation step will be made in the top furnace of our MultiDip simulator, schematically represented in Figure 3. The oxidized surface will be characterized by GDOS (selective oxidation and oxide thickness) and XRD (type of iron oxide).
- In a second step the full annealing cycle will be performed in the bottom furnace of the Multidip simulator, with again a low (-30°C) or a high (0°C) dew point, with or without an oxidation step. The idea here is to determine if the selective oxidation mode can influence the selective oxide repartition under the reduce iron layer. Indeed, a previous work made during the ZCO54 study (Figure 4), has clearly indicated that the repartition of the selective oxidation at the end of the annealing cycle can strongly deteriorate the adhesion of the zinc coating. The fully annealed surface will be

characterized by Scanning Auger (selective oxidation repartition) and GDOS (more in depth and decarburizing analysis).

- In a third step, the samples will be dipped in a Zn+0.25%Al bath at 460°C during 3s. A zinc flow will be established along the panels as schematically represented in Figure 5. The coating adhesion will be characterized by a 1T bending test with tape application. In case of bad coating adhesion, the weak coating/steel interface will be characterized by Scanning Auger analysis. The inhibition layer will be observed by SEM, after an electrochemical zinc stripping. GDOS can be made to compare the amount of Fe_2Al_5, but the remaining selective oxidation between the grains of Fe_2Al_5 will be dissolved during the electrochemical dissolution.

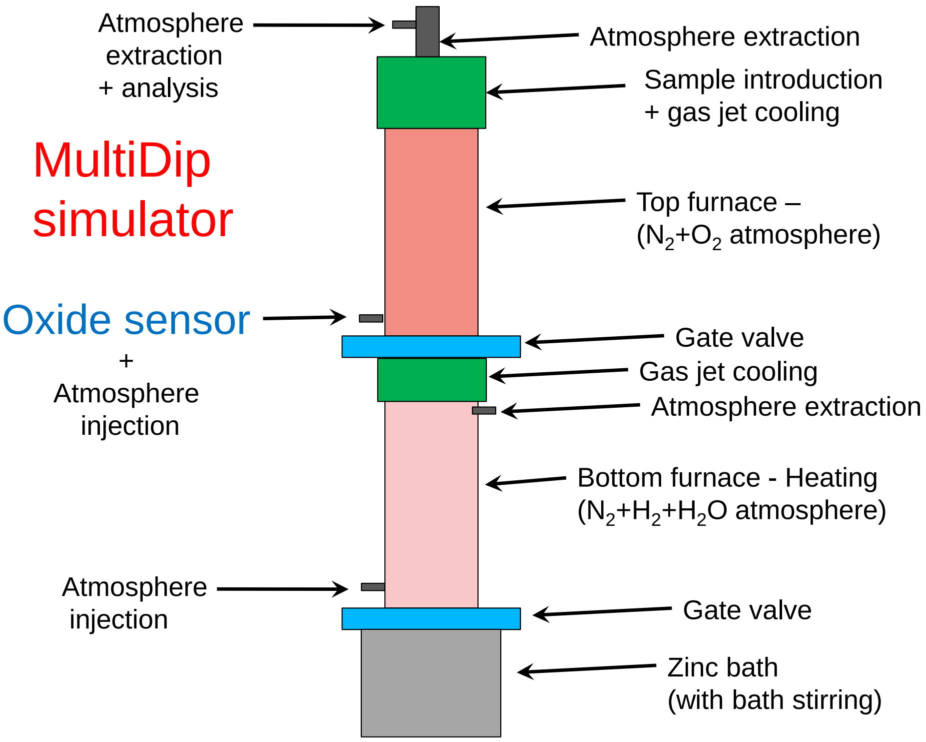

Figure 3: Schematic view of the MultiDip simulator allowing to perform an oxidation step in the top furnace during an annealing cycle made in the bottom furnace.

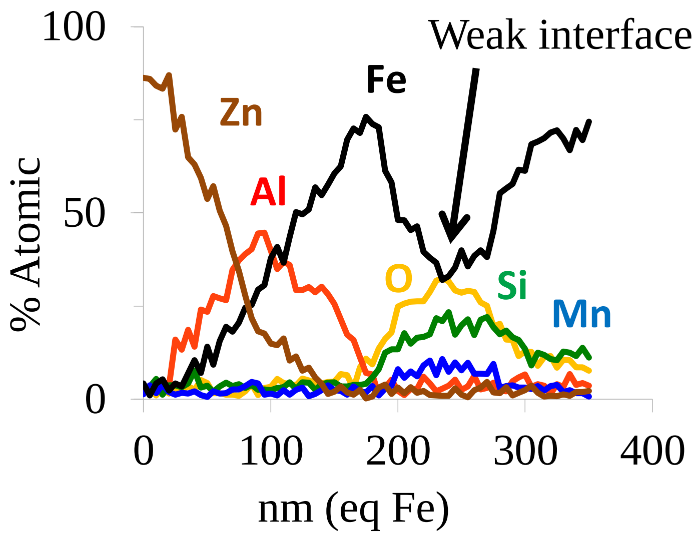

Figure 4: Scanning Auger analysis showing the presence of thin SiO_2 layer at the steel / coating interface after an oxidation/reduction process, which completely deteriorate coating adhesion (from ZCO-54 study)

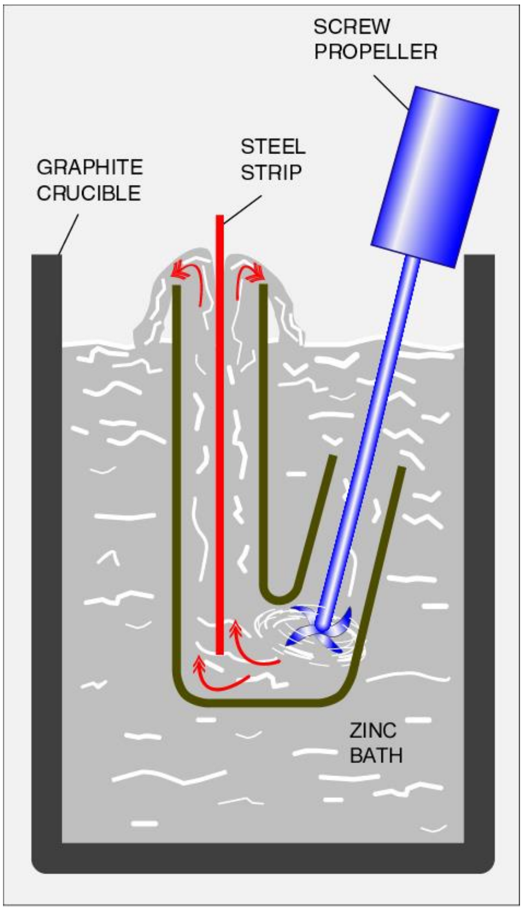

Figure 5: Schematic view of the zinc stirring system allowing obtaining a zinc flow of 0.4 m/s along the steel sample.

2.2.2 Zinc wetting experiments

The zinc wetting will be quantified by sessile drop experiments. The annealing simulations will be made in the glove box where the wetting measurement is also installed. However, as it is not possible to obtain a homogeneous iron oxide thickness on the small samples used for the wetting experiments (20x30mm), the oxidation step will be made in the MultiDip simulator on 100x200mm panels. Smaller samples will cut out of these panels to prepare the samples for the wetting experiments.
The zinc wetting experiments will be made for a zinc droplet/sample temperature of 440°C / 460°C and 480°C. 3 tests will made for the same annealing condition.

2.3. Deliverables:

Reports will be written semi-annually and annually.

2.4. Project Team Makeup — Qualifications and Facilities Description:

Centre for Research in Metallurgy (CRM) is a collective research centre having as core members two major worldwide steel companies (ArcelorMittal and Tata Steel) and as associated members numerous companies producing metals, providing services to the steel industry or promoting the use of metallic products. The specific skills for this project are related to expertise in gas-metal reactions, associated with reactivity between materials. Therefore, Dr L. Bordignon, as scientific expert with more than 30 years of experience in these fields, will be in charge for overseeing all trials and analyses. The continuous study follow-up will be made by Dr D. Debrabandere, who is also familiar with hot dip galvanizing.
Finally, the Auger analyses are made by P Bastin, which has more than 25 years of experience in this specific field.

2.5. Costs:

Description	1st Sem	2nd Sem	3rd Sem	4th Sem	5th Sem	6th Sem	Costs (USD)
1. Steel composition							500
2. MultiDip trials							
2.1. Characterisation after the oxidation step							15.000
2.2. Characterisation after full annealing							55.000
2.3. Characterisation after hot dipping							39.500
3. Wetting experiments							60.000
4. Reporting and traveling							10.000

2.6 Time schedule

The work will be carried out in a 3-year period beginning in March 2017.