

## Non-Oxidizing Water Quench to Tailor UHSS for Excellent Zinc Wettability

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Recently, Fives Stein has developed a non-oxidizing wet cooling process dedicated to high strength steel quenching in continuous galvanizing lines to freeze desired bainite and martensite phases, triggering Tata Steel R&D to collaborate in an innovative project together with Fives Stein. They have demonstrated that this promising technology could improve metallurgy and coatability. This technology can be implemented for galvanizing 3rd generation Advanced High Strength Steel (AHSS) / Ultra High Strength Steel (UHSS) grades of Tata Steel. The pickling effect of wet cooling agent (water containing an acid) on steel surface after annealing prior to dipping into the Zn bath according to the wet cooling concept developed by Fives Stein was assessed by a metallurgy driven set of experiments on a Non-Oxidizing-Water-Quench (NOWQ) cooling test bench simulation. Selected samples were further preheated to required temperature in 5%H<sub>2</sub>/N<sub>2</sub> and subsequently dipped in liquid zinc by a hot dip zinc simulator HDAS (Heat to Coat heated, i.e., without annealing). Results of experiments along with X-ray Photoelectron Spectroscopy (XPS)/Glow Discharge Optical Emission Spectroscopy (GDOES) analyses demonstrated that the NOWQ technology significantly improved pickling efficiency of Mn, Si, and Al selective oxides to secure good Zn wetting of exposed metallic strip surface.

**Keywords:** Non-Oxidizing-Water-Quench, Galvanizing, Wettability, AHSS

### 1. Introduction

The automotive steel market tendency for higher strength steel grades is accelerating today, and a large variety of 3<sup>rd</sup> generation AHSS / UHSS grades are developed in which, besides yield strength, other properties are also considered, like local and global formability. From one side the production of galvanized 3<sup>rd</sup> generation AHSS / UHSS grades in a continuous processing line requires a proper cooling control [1] to follow the required thermal cycles for each grade and from the other side requires a clean (metallic) steel surface after continuous annealing prior to hot-dipping, to secure a good surface quality for stable galvanizing production of first choice products.

The Non-Oxidizing Wet Flash Cooling (NOWFC) technology developed by Fives Stein [2] attracted the attention of Tata Steel as it is claimed that this technology secures a stable production of first choice products with improved flatness and a good surface quality for galvanized

products (see Fig. 1).

Intermediate water quenching in a Continuous Annealing Processing Line (CAPL) is a method for production of uncoated UHSS. Mn and Si, the most important alloying elements for the 3<sup>rd</sup> generation, might form mixed Mn,Si-oxide at the external steel surface during the annealing step, because of the annealing atmosphere within the furnace, which is slightly oxidizing to alloy elements. The selective oxides formed may be removable by using pH 2 water instead of de-ionized water. In that case, there is an intermediate pickling action.

Fives Stein has installed a test bench equipment for annealing steel samples combined with fast cooling/pickling (Non-Oxidizing Water Quench) at Bar le Duc in France (Fig. 2).

The samples at intermediate stage (after cooling or after overage) were brought to IJmuiden in the Netherlands, Tata Steel R&D, for XPS and GDOES measurements. Some of the samples were dipped in liquid zinc by a state of the art Hot Dip Annealing Simulator (HDAS) without annealing step (i.e. just Heat-to-Coat) in order to check the surface quality.

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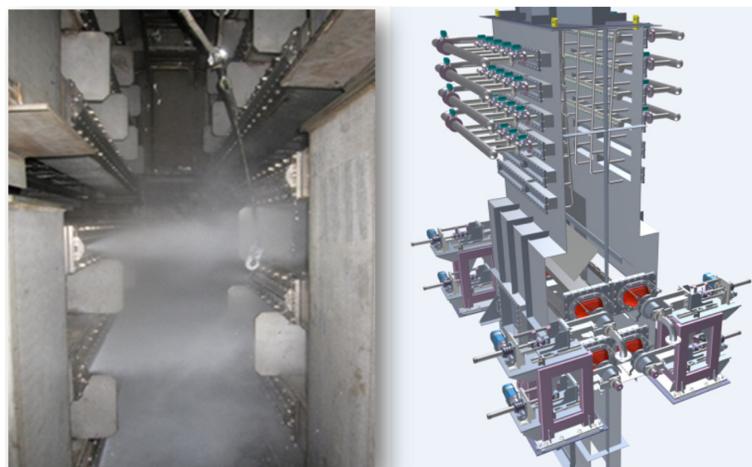


Fig. 1. A camera image of commercial cooling section (left) and 3D Computer Aided Design image (right) that demonstrate the water jets at each side according to the Non-Oxidizing Wet Flash Cooling (NOWFC) technology developed by Fives Stein [2-3]

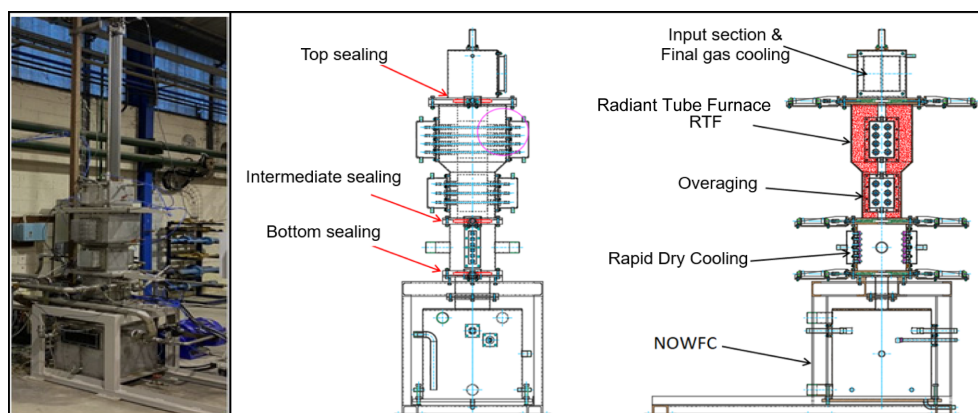


Fig. 2. Non-Oxidizing Water Quench (NOWQ) test bench at Bar le Duc in France, Fives Stein

Table 1. Table with grades 1, 2 (dual phase steel DP600) and 3; level of milli wt% of Mn, Si and Al chosen for the experiments used in this study

Grade #	Mn	Si	Al
1	2060	440	600
DP600	1800	250	-
3	2901	1261	32

## 2. Experimental

Different chemistry levels of Mn, Si and Al have been selected in order to test the surface quality at different process stages: after annealing, after NOWQ, after overage and after hot dip in liquid Zn. In Table 1 three of the selected chemistries are given in milli wt% content of Mn, Si and Al chosen for these experiments.

### 2.1 First set of experiments

The first set of experiments was conducted in reducing annealing atmosphere using a maximum top annealing temperature of 870 °C (at 4% H<sub>2</sub> and dew point -30 °C in order to simulate maximum external selective oxidation which can take place as a result of Mn, Si diffusion to the surface) and prove the pickling effect of the NOWQ quench by XPS measurements. The quench end temperature was varied between 400 °C and T < 100 °C.

Three different atmosphere conditions were chosen during cooling:

1. dry cooling by N<sub>2</sub>
2. wet cooling with no pickling agent
3. wet pickling with pickling agent (2% formic acid – FA).

The annealing cycle used in the Fives Stein test bench is given in Fig. 3a. The samples were investigated by XPS

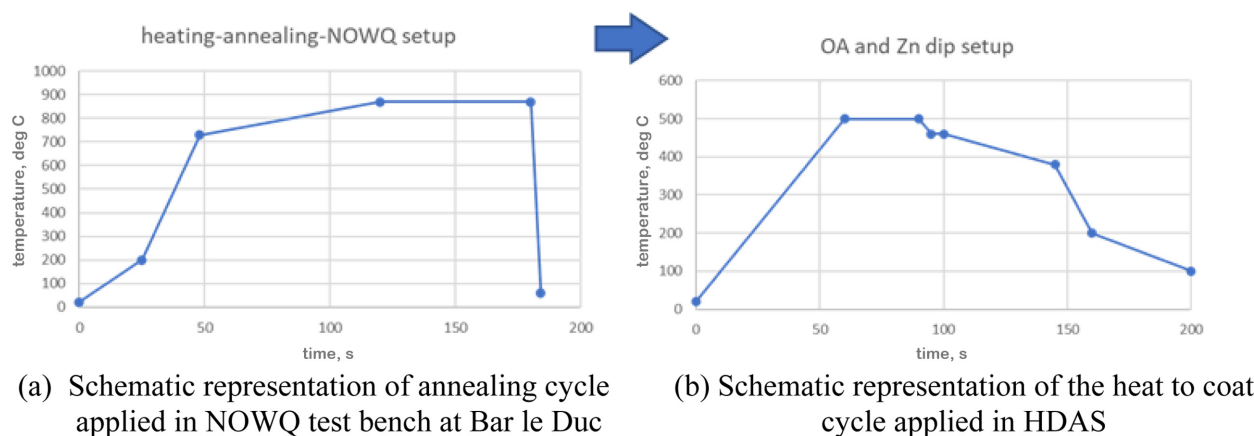


Fig. 3. Schematic representation of annealing cycle applied during the first set of experiments; the arrow indicating exposure to air

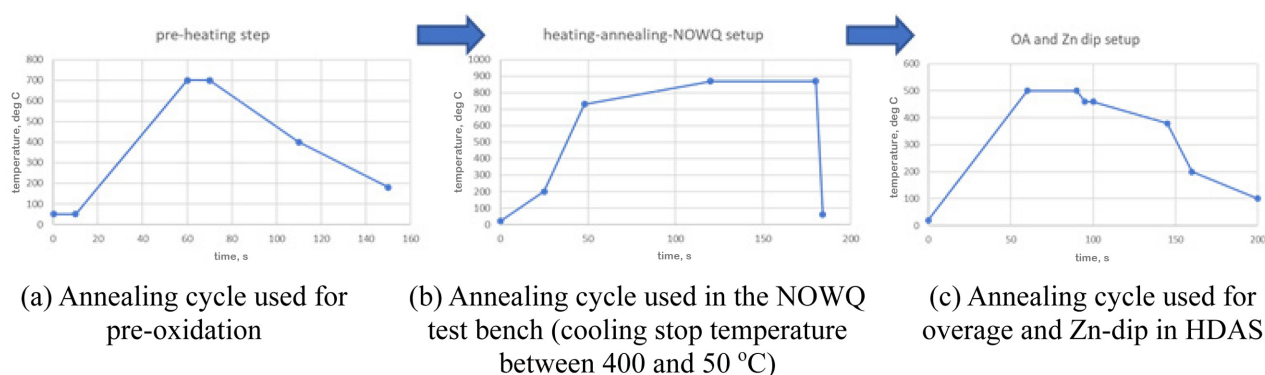


Fig. 4. Schematic representation of the second set of experiments, the arrows indicating exposure to air

after this step.

All samples were taken out of the test bench dry and stored in sealed plastic bags together with a silica gel for transport to IJmuiden. Growth of a (thin) native iron oxide layer was therefore unavoidable, but growth of hydroxide was avoided this way.

A very limited number of samples were subjected to a heat-to-coat (reductive) reheating cycle and hot dip galvanization with HDAS (Fig. 3b). In this Heat to Coat cycle, we aimed for reduction of iron oxide (grown during transport) without reducing any of the external selective oxide particles or film (grown during soak).

## 2.2 Second set of experiments

For the second set of experiments (Fig. 4) samples were first annealed at Tata Steel in HDAS simulator in order to pre-oxidise the samples prior to NOWQ, to simulate the atmosphere, as recently used by steel manufacturing for heavy alloyed UHSS as standard procedure in order

to limit the external selective oxidation of Mn or Si [3]. The annealing step simulated a direct furnace flame, heating from 20° to 700 °C at a linear rate of 10 °C/s; soaking for 10 sec at 700 °C in  $N_2 + 1800 \text{ ppm } O_2$  and dew point +10 °C followed by cooling with dewpoint -60 °C  $N_2$  (Fig. 4a). After pre-oxidation, samples were transported to Bar le Duc and annealed in the test bench to the top temperature of 870 °C with a dew point of -10 °C and quenched to final temperature of either 400° or  $T < 100 \text{ °C}$  (Fig. 4b). Three different atmosphere conditions were chosen:

1. dry cooling ( $N_2$ )
2. wet cooling with no pickling agent
3. wet pickling with pickling agent (2% formic acid – FA).

The samples were transported to Tata Steel R&D using the same procedure as in the first set of experiments. The samples received an overage treatment (OA either -20 °C or -60 °C) (Fig. 4c) and XPS measurements were performed. Some of the samples were galvanized.

The steel surface after the pre-oxidation step was examined by GDOES. The steel surfaces after treatment in the NOWQ test bench were investigated by XPS. A limited number of samples was subjected to overage and hot dip galvanization with HDAS. In this Heat to Coat cycle, we aimed for reduction of iron oxide (grown during transport) without reducing any of the external selective oxide particles or film (grown during soak). The uncoated part of the surface above zinc level was characterized by XPS.

XPS spectra were acquired using a Kratos Axis Ultra DLD instrument in hybrid mode with magnetic lens on. A monochromatic Al K $\alpha$  X-ray source was used at 15 mA and 15 kV to generate the X-ray photons of 1486.7 eV and the emitted photoelectrons were collected from the slot area of  $0.7 \times 0.3 \text{ mm}^2$ . The base pressure in the analysis chamber along the spectra acquisition was stable at  $3 \times 10^{-10}$  mbar. The as-received samples (unpacked from the sealed plastic bag) were mounted on a stainless steel sample bar with Cu strips to avoid a positive charging as a result of the emitted photoelectrons. The conditions

used for all of the survey scans were as follows: energy range 0 - 1200 eV, pass energy of 160 eV, step size of 1.0 eV, sweep time of 180 s. The high-resolution spectra were acquired within an energy range of 40–20 eV, depending on the peak being examined, with a pass energy of 40 eV and a step size of 0.1 eV.

The acquired XPS spectra were processed and quantified using Casa XPS software. The energy was calibrated using the adventitious C 1s peak to a fixed value of 284.8 eV. After calibration, the background from each spectrum was subtracted using a Shirley background to remove most of the extrinsic loss structure. All survey scans were analysed to determine the stoichiometry of the compound by using the appropriate sensitivity factors and to determine the amount of adventitious carbon and contaminates present.

### 3. Results and Discussion

#### 3.1 First set of experiments results

An example of the annealing cycle realised during the

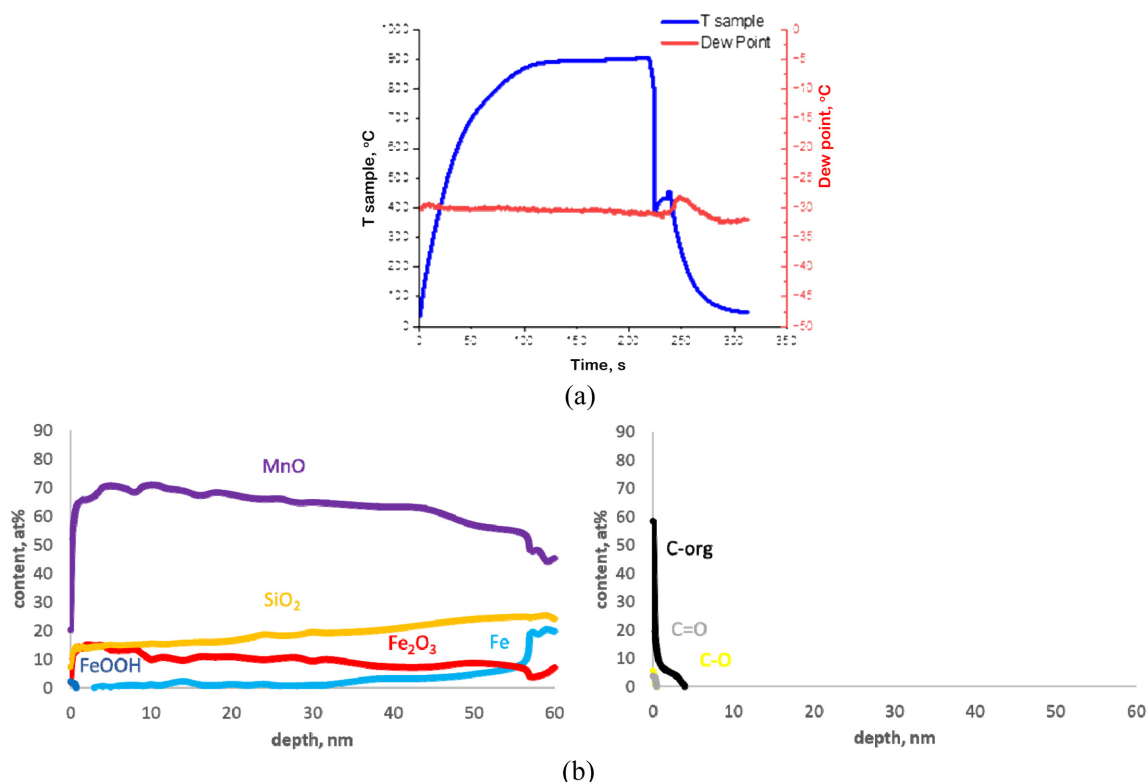


Fig. 5. (a) Example of annealing and cooling rate achieved during first set of experiments –  $T_{\text{final cooling}} = 400 \text{ }^{\circ}\text{C}$ , (b) XPS depth profiles of steel grade 3 after transport to Tata Steel R&D,  $T_{\text{final cooling}} = 400 \text{ }^{\circ}\text{C}$



first test bench experiments at Fives Stein is given in the Fig. 5a showing that we could realise the aimed temperatures and dew points as intended. The rapid cooling by water is suddenly stopped when the sample reaches 400 °C. From then on some temperature rise due to transformation heat. The sample is brought to another chamber where pure nitrogen gas is blown onto the sample to forcefully dry and cool it. That way, the build-up of a fresh (thermal) oxide layer is prevented. As one can see the cooling rate by cooling with a stream of gas is not very fast. The oven is opened and the sample is exposed to air after the sample reaches about 50 °C.

The XPS results (Fig. 5b) of grade 3 (highest alloying level) after quenching at 400 °C show a high enrichment of  $Mn_xO_y$  (60-70% content), 15%  $Si_xO_y$  and only 15% content of  $Fe_2O_3$ . The depth of the oxide on the surface is more than 60-70 nm. The reduction atmosphere during annealing facilitates the external oxidation to Mn,Si-oxide as intended. These oxides are detrimental for zinc wetting and subsequent growth of a uniform inhibition layer, moreover Mn,Si-oxides are not reducible in the overage section at 500 °C in  $H_2$ .

The reason of the presence at the surface of the  $Mn_xO_y$  is that the temperature is above the Leidenfrost temperature [4] and therefore the liquid (electrolyte) does not touch the strip and no pickling effect is observed.

The second type of annealing considers cooling to far lower temperature ( $T < 100$  °C), in which case the strip is in contact with the liquid (see Fig. 6a). Perhaps it is visible that during very rapid water cooling the rate of cooling near 300 °C is slightly lower due to transformation heat from the steel. After reaching  $T < 100$  °C the water spray stops. The excess of water from the sample surface was removed as fast as possible by moving the sample to another chamber where dry nitrogen was applied. Probably, the temperature of the gas in the initial (wet) chamber is higher than the temperature of the sample after cooling. That is why the sample warms up slightly until 310 °C. After reaching the next chamber there is a rise in temperature before cooling with  $N_2$  gas starts. We don't know about the "hick-up" of the temperature at 315 °C. This feature is not considered relevant for the results.

The XPS results (Fig. 6b) of grade 3 after quenching to below the Leidenfrost temperature show only 5-6 nm

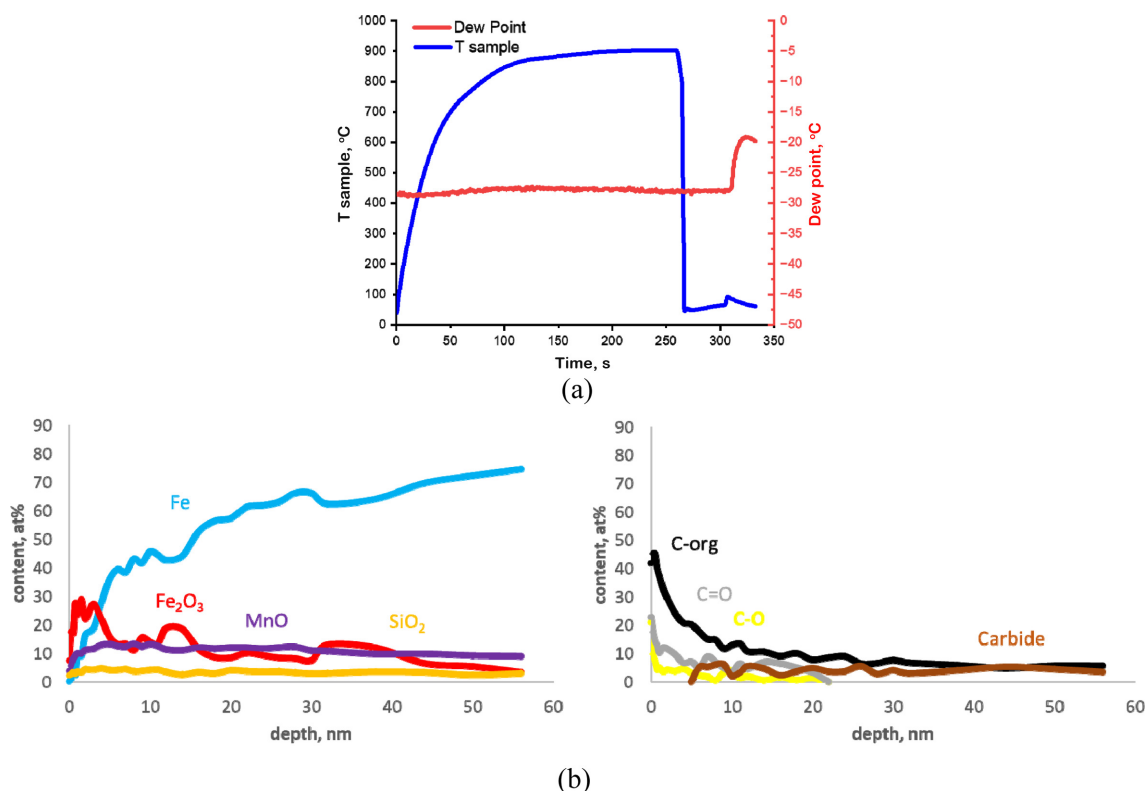


Fig. 6. (a) Example of annealing and cooling rate achieved during the second set of test bench experiments at Bar le Duc –  $T_{final\ cooling} < 100$  °C, (b) XPS depth profiles of steel grade 3 after transport to Tata Steel R&D,  $T_{final\ cooling} < 100$  °C

$\text{Fe}_2\text{O}_3$  present at the surface, which is the result of oxidation during transport and or handling of the samples towards the XPS apparatus. The Leidenfrost effect [4] is the core aspect of this process and the Leidenfrost temperature  $T_{\text{Lei}}$  mainly depends on the water density projected on the strip, on the water pressure/droplets size and on the water temperature. From strip annealing temperature to  $T_{\text{Lei}}$ , a vapour film on the hot steel surface (film boiling regime) prevents the dissolution and removal of oxides but protects the strip from excessive thermo-mechanical constraints which may results in flatness issues. At lower surface temperature below  $T_{\text{Lei}}$  (transition and nucleate boiling regimes), the pH 2 liquid water touches the surface, thereby dissolving and removing selective alloy oxides, and preventing the formation of iron oxide. Just before the next (dry) stage a thin layer of iron formiate (salt of formic acid) is deposited which passivates the surface.

Hot dip simulations in HDAS at Tata Steel show similar results regarding galvanized surface quality. In Fig. 7 the steel grade 3 samples are shown after annealing and cooling (top row) and after dipping in Zn for four different conditions:

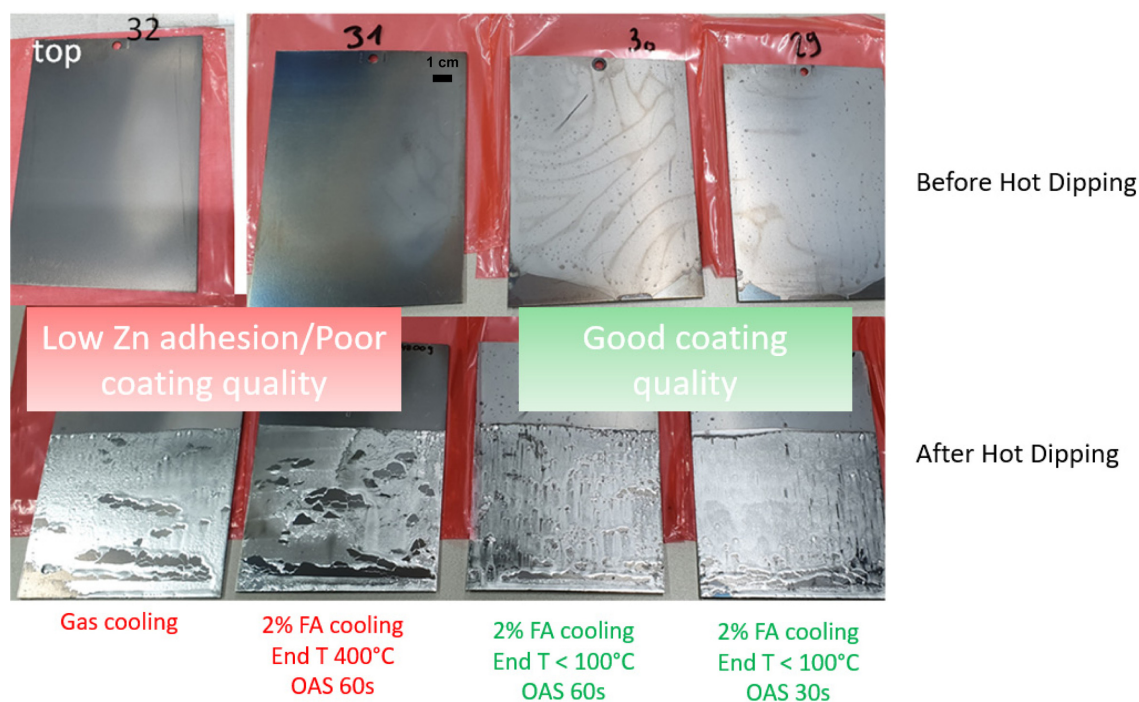
- gas cooling (reference state - actual conditions in HDG lines): *low Zn adhesion / poor coating quality*

- NOWQ to 400 °C using pickling agent (2% formic acid) and an overaging time of 60 sec: *low Zn adhesion / poor coating quality (cooling end temperature in the film boiling regime, no contact with steel strip)*
- NOWQ to  $T < 100$  °C using pickling agent (2% formic acid- FA) and an overaging time of 60 sec: *good coating quality (cooling end temperature in the nucleate boiling regime  $T < T_{\text{Lei}}$ )*
- NOWQ to  $T < 100$  °C using pickling agent (2% formic acid- FA) and an overaging time of 30 sec: *good coating quality*

Visual inspection shows that the pickled surfaces, even when exposed to air during storage, were wettable by liquid zinc after the overage treatment.

The results are very similar for all steel grades including the highest alloyed materials.

In order to check if a native iron oxide layer of a few nm can be reduced in the overage section we treated an interstitial free steel directly in the reaction cell, that is directly attached to the XPS instrument, with air for 5 min and 30 min. The XPS spectroscopy demonstrated the presence of native  $\text{Fe}_2\text{O}_3$ . Afterwards the sample was treated at 600 °C for 3 min in ultra-high vacuum (UHV) and at 450 °C for 1sec in UHV. The XPS results show that



**Fig. 7. Optical surface appearance of the samples after NOWQ without and after dipping in Zn bath for four different conditions – steel grade 3 (each sample is 12 cm in width)**

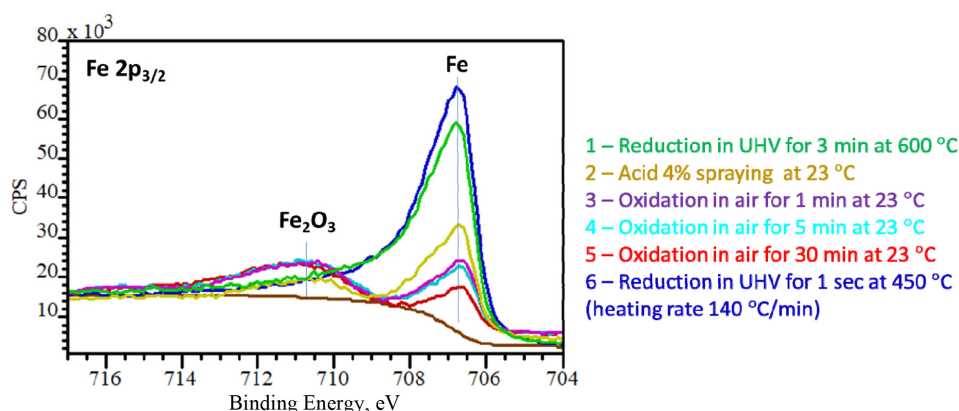


Fig. 8. XPS Fe 2p<sub>3/2</sub> spectra of the interstitial free steel oxidized in different conditions and after reduction in UHV, latter to confirm the Fe<sub>2</sub>O<sub>3</sub> oxide reduction and formate layer removal in overage conditions

the film layer of a few nm of native Fe<sub>2</sub>O<sub>3</sub> formed by oxidizing in air can be reduced during overaging, resulting in fresh Fe surface which can be easily galvanized (see Fig. 8).

### 3.2 Second set of experiments results

The second set of experiments is dedicated to steel grades which do not need to be cooled to temperatures in the nucleate boiling regime (i.e. to below 150 °C). A pre-oxidation treatment was given to prevent external selective oxidation of Mn/Si-oxides on those AHSS-grades that have a cooling stop-T above 300 °C (not wetted by dilute acid solution). After pre-oxidation an oxide layer was formed, FeOx, of 120 nm for grade 1 and 130 °nm for regular dual phase steel DP600 (Fig. 9).

Fig. 10b shows that after cooling to 400 °C, the sample is still covered by a thick layer of FeOx (containing low amount of MnO as well). Apparently, the annealing condition during the second test bench of experiments did not reduce FeOx formed by pre-oxidation, and NOWQ to 400 °C did not remove FeOx. Most probably the dew point of -10 °C combined with a short annealing was not sufficient. In practice in a real hot dip galvanizing (HDG) for each steel grade only a few nm of Fe<sub>x</sub>O<sub>y</sub> layer is formed during pre-oxidation so that at the end of full radiant tube section the oxide layer is reduced.

Fig. 10c shows wetting for more than 70% of the surface or surface with many not wetting spots, which is in agreement with XPS spectroscopy results which

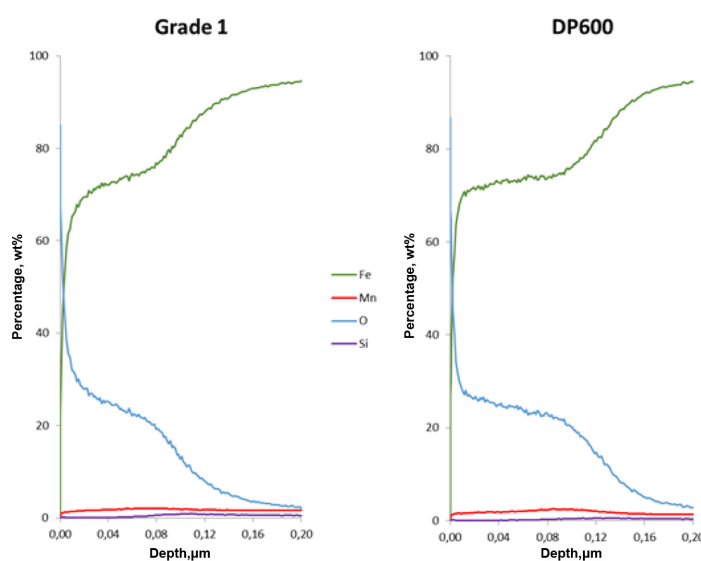


Fig. 9. Fe<sub>2</sub>O<sub>3</sub> thickness measured by GDOES after pre-oxidation of grade 1 and DP600

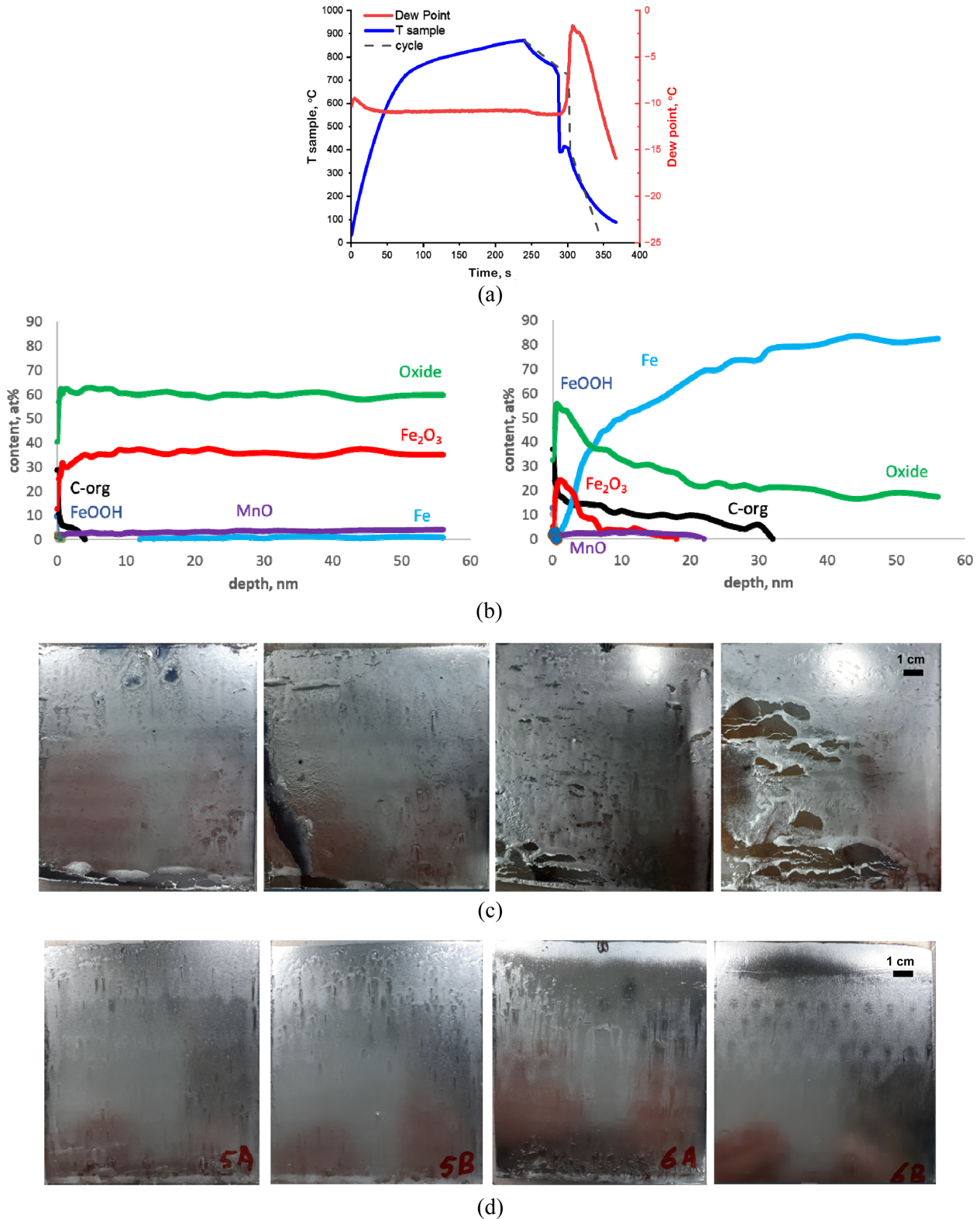


Fig. 10. (a) Example of the annealing and cooling cycle achieved during the second set of test bench experiments to quench end temperature 400 °C at Bar le Duc, (b) XPS depth profiles of steel grade 1 after transport to Tata Steel R&D and cooling to 400 °C (left) and T < 100 °C (right), (c) Surface quality aspect of the samples after overaging and hot dip galvanizing of grade 1 (2 at the left) and DP600 (2 at the right) samples cooled to 400 °C (each sample is 12 cm in width), (d) Surface quality aspects after overaging and galvanizing of grade1 (2 at the left) and DP600 (2 at the right) cooled to T < 100 °C (each sample is 12 cm in width)



confirmed that FeO layer was not reduced in the experimental condition applied. Previous experimental results in XPS (Fig. 7) demonstrated that during overage we can reduce  $\text{Fe}_2\text{O}_3$  which may possible form during cooling with NOWQ. Therefore, it is important that for the steel grades with high alloying elements and a required cooling end temperature above 300 °C similar precaution must be taken as for dry atmosphere cooling sections because NOWQ does not show extra advantages for pickling effect.

Fig. 10d proves once more the results observed in Fig. 7 that cooling to below the Leidenfrost temperature cleans the surface of any oxide layer formed before by the pickling effect of the formic acid present used during NOWQ step, followed by passivation of the surface by iron formiate. Combination of pre-oxidation and NOWFC with  $T < 100$  °C gives the best results in terms of coatability.

#### 4. Conclusions

It turned out that pickling in the cooling phase is possible, but only when the cooling stop temperature is low enough for liquid diluted acid to touch the strip. In that case, oxides are rapidly dissolved and removed; and just before drying the steel surface is passivated by a thin layer of iron formiate. The pickling effect is proven for high alloyed chemistry with 2.9 wt% Mn and 1.25 wt% Si in the most critical annealing situation, when selective external oxidation was favoured.

For low to medium alloy content steel grades, in case one chooses a cooling end temperature in the film boiling regime (typically higher than 350 °C), one needs the normal precautions to prevent external selective oxidation of alloy elements, like pre-oxidation followed by reduction.

In our experimental facility 130 nm FeOx applied on the surface prior to annealing in the NOWQ bench could not be reduced to ferrite before quenching in the NOWQ section. Therefore, the surface quality of the galvanized surface showed good wetting behaviour only after removal of iron oxide by NOWQ pickling. Experiments performed in the XPS machine show that the >10 nm thin

$\text{Fe}_2\text{O}_3$  layer, which may form during NOWQ, can be reduced in the overage section.

It is proven that Non-Oxidizing Wet Flash Cooling can be used for 3<sup>rd</sup> generation AHSS / UHSS in a galvanizing line showing the same benefits as for continuous annealing lines (CAL) regarding flexibility of cooling rates and flatness and on top of it can provide beneficial effects for surface quality and coatability. Combination of pre-oxidation and cooling in NOWFC section to low temperature (T in nucleation boiling regime) gives the best results for highly alloyed steel grades such as 3<sup>rd</sup> generation AHSS.

In the industrial case, the galvanizing line will be equipped with pre-oxidation capability, a dry cooling section followed with a Non-Oxidizing Wet Flash Cooling section in order to process the whole range of steel grades in a flexible manner. The dry cooling technology can use high  $\text{H}_2$  atmosphere depending on process requirement to reach high cooling rates up to 200 °C/s/mm for some grades, while the combination of dry cooling and wet quenching can be used for the more complex steel grades as the 3<sup>rd</sup> generation AHSS grades.

#### Acknowledgements

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