New environmental friendly hot rolled steel suitable for two sides enamelling intended for the manufacture of silos and tanks

Presenting Philippe Gousselot*, Co-author Ulrike Lorenz‡

*: ArcelorMittal R&D – 17, Avenue des Tilleuls – F-57190 Florange – France – philippe.gousselot@arcelormittal.com
‡: ArcelorMittal R&D Gent OCAS N.V. – Technologiepark 935 – BE 9052 Zwijnaarde – ulrike.lorenz@arcelormittal.com

Abstract

ArcelorMittal has developed a new environmental friendly hot rolled enamelling steel grade suitable for two-sides enamelling and intended for the manufacturing of tanks and silos. This market is currently growing and, up to now, there was no existing steel answering properly the necessary requirements in term of mechanical properties after enamelling and fishscale resistance.
Tanks and silos manufacturers are at the moment implementing high strength low alloyed steel grades which present at least two drawbacks:

- Steels require high strength level after enamel firing to withstand the pressure of the load contained in the silo. However, high temperature enamelling process leads to strength loss and contributes to hydrogen absorption in the steel.
- In order to obtain good enamel adhesion and reduce the risk of fishscaling, it is necessary to use ground enamels or sublayers strongly doped with metallic oxides such as NiO or CoO, for which the new European regulations relative to the environment strongly threaten the use.

ArcelorMittal is now proposing a new steel grade called S390EK which allows circumventing these disadvantages while leading to some savings for the end user. A good fishscale resistance combined with minimum yield strength of 390 MPa is guaranteed after two sides enamelling when using Ni-free enamels. This development is based on a high-titanium steel concept; titanium carbide precipitates, contained in the steel, act as irreversible hydrogen traps and are responsible for the high strength after enamelling. A highly controlled processing is required in the hot strip mill in order to promote the formation of the aimed precipitation system. We will describe in this presentation the mechanism involved and show you how it has enabled us to develop the first hot rolled steel suitable for two sides enamelling, compliant with future environmental legislation, and also leading to savings in the whole manufacturing process.

Introduction

The use of silos and tanks is now widely spread in agricultural, municipal and industrial domains for different applications such as:

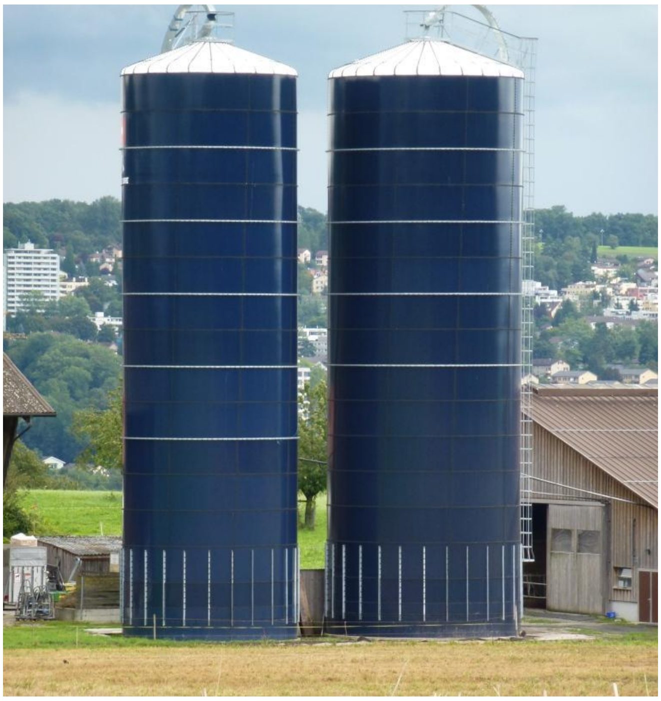
- Safe containment of solid and liquid material such as grain (dry or moist), forage, agricultural slurry
- Biogas production and methanization
- Drinking water, wastewater treatment, effluent storage, sewage treatment
- Industrial effluents storage and treatment

Different materials can be used for their manufacturing:

- Hot dip galvanised steel
- Epoxy coated material
- Concrete
- Stainless steel
- Enamelled steel on hot rolled substrate

Compared to the other materials, the use of enamelled steel panels for silo manufacturing offers multiple advantages in term of durability and represents the best compromise between cost and sustainability. Moreover, because of the modular conception of the silo, build time is reduced and therefore, maintenance costs are reduced.

The changes in regulations related to the environment and the willingness of countries to support them, favours the development of this kind of equipment, especially for the treatment of industrial and agricultural effluents. It could therefore favour an increase in the demand for hot rolled enamelling steel in the coming years. Hot rolled steel intended for such use must be suitable for two sides enamelling and present a high level of mechanical properties after enamel firing so as to withstand the pressure of the load contained in the silo or tank. However, steel grades that exactly meet these specifications, especially two sides enamelling ability without requiring specific surface treatment, do not currently exist on the market. HSLA steel grade are already used for this application, but, as they are normally not suitable for two sides enamelling, it is necessary, in order to obtain good enamel adhesion and thus reduce the risk of fishscale appearance, to beforehand coat the steel surface with enriched metallic oxide sub-layer or to use strongly metallic oxide doped ground enamels, which runs counter to the new environmental regulations, in particular REACH and food compliance, aiming at more or less short term, to ban the use of nickel and cobalt oxides. Therefore, ArcelorMittal has developed a new steel grade S390EK, suitable for two sides enamelling without requiring the use of a special surface treatment or use of strongly doped enamel with adherent oxides and presenting a minimum level of yield strength of 390 MPa after enamel firing.



Why developing a specific steel grade for this application?

Enamelled steel is perfectly designed for silo and tank manufacturing

Various types of materials can be used for the manufacture of tanks and silos, especially concrete, galvanized steel or stainless steel. If galvanized steel and concrete are relatively well suited for the storage of dry matter, this is not the case for the storage of wet contents which generates acid issued from the fermentation which can attack these materials. Moreover, stainless steel is quite expensive for this kind of application. Enamelled steel, obtained through the association at high temperature, of a steel substrate and a glass (enamel) has outstanding properties, especially regarding chemical resistance (resistance to acids and alkali). Therefore, this is a choice product for the manufacturing of silos and tanks and is an excellent compromise between quality, in-use properties, and costs. In addition, the enamel being applied on both sides, outside of the silo will be protected from the bad weather and its lifespan will be extended as well: it will not be necessary to change panels after years of use. The manufacture of silo requires the use of heavy gauge steel, usually between 2 and 10 mm, and having a high level of yield strength to withstand the pressure of the load contained in it.

However, there is currently no steel fitting exactly these characteristics

There is currently no existing hot rolled steel grade dedicated for this application, suitable for two sides enamelling and having such a level of mechanical properties. Typically, silo manufacturers use high strength steels, such as S420MC, S460MC or S700MC. These grades are normally not dedicated for 2 sides enamelling because there is a high risk of fishscale appearance after enamel firing. A way to limit this defect is to increase enamel adhesion on steel. This can be obtained by using sub layers or ground enamel strongly doped with adhesion metallic oxides (NiO or CoO). Nevertheless, new regulations on environment (REACH and regulation related to food compliance) threaten at more or less short term the use of nickel and cobalt oxides in enamel, so that this option may soon no longer be usable.

Metallurgical aspects

A specific metallurgy is required to avoid fishscales

The fishscales are caused by the difference in hydrogen solubility in the steel during enameling firing and subsequent cooling. As shown in Figure 1, the hydrogen solubility increases with increasing temperature and even faster when ferrite (α) transforms into austenite (γ). During enamel firing, hydrogen produced by the decomposition of humidity contained in the furnace and the enamel penetrates in the steel. Once the material is cooled, the solubility of hydrogen in steel decreases and it migrates towards the steel/enamel interface and is no longer able to escape since the enamel has solidified. Hard enamel layer will break in form of fishscales, due to the high pressures generated by the oversaturation of diatomic hydrogen at the interface. To avoid the fishscaling formation, the steel must have a sufficiently large hydrogen absorption capacity. This is obtained by creating hydrogen traps in the steel, particularly irreversible (permanent) traps. Conventionally, the hydrogen trapping effect is obtained in cold rolled material by physical traps; breaking-up the cementite particles during cold rolling operation produces cracks which are effective for hydrogen trapping. In the hot rolled material, the physical trapping is almost impossible and therefore chemical traps (precipitates) or attractive traps (stress fields created by the presence of imperfections) must be used for the same purpose.

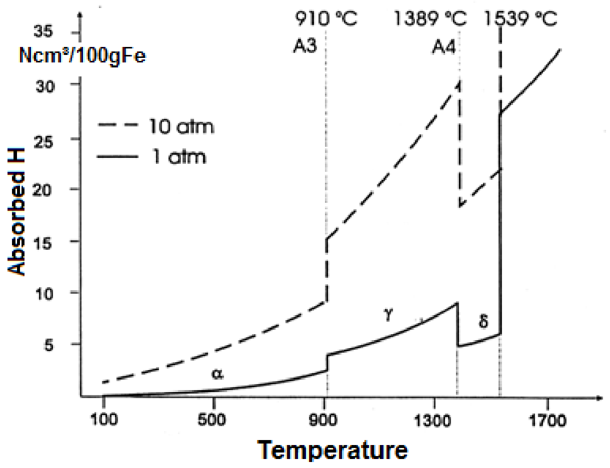


Figure 1: Solubility of hydrogen as a function of temperature and pressure

How to get very effective hydrogen traps with hot rolled steel?

The major trapping effect is given by coherent and semi-coherent particles. The interface between the precipitates and the ferrite steel matrix provides hydrogen trapping sites in the stress fields of the dislocation misfits. The effectiveness of hydrogen trapping decreases if the coherence of precipitates increases. In hot rolled steels, there are different types of more or less efficient hydrogen traps, i.e. temporary (reversible) traps and permanent (irreversible) traps. Interstitial atoms such as B or N are reversible traps and release hydrogen and therefore have a limited efficiency. On the other hand, precipitates such as BN, TiS, $Ti_4C_2S_2$, TiC, Ti(C,N) and TiN are highly effective irreversible traps at which fine, coherent TiC are reported most relevant [1]. Furthermore, at ambient temperatures coherent and semi-coherent NbC and VC nano-precipitates show a hydrogen trapping ability like that of TiC and varies in the descending order of NbC>TiC>>VC. At high temperatures, in contrary to TiC, incoherent NbC and VC are unable to trap hydrogen [2]. Coherent and semi-coherent alloy carbides trap hydrogen at the precipitation/matrix interface, which means the trapping ability increases the larger the number and finer the particles are [3].

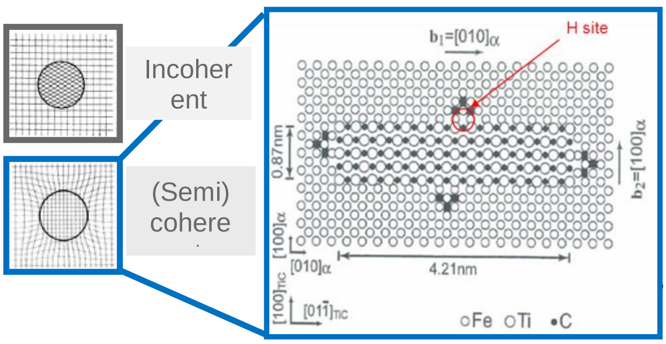


Figure 2: incoherent and coherent state: coherent precipitates are aligned with crystallographic lattice

High level of Ti and low level of C is required for hot rolled steel suitable for 2 sides enamelling

A balance of high levels of Ti and low levels of C is required in the steel to form sufficient hydrogen trapping sites in the ferrite phase. A high titanium level (≥0.18%Ti) is necessary to fix the carbon through the precipitation of Ti4C2S2, Ti(C,N) and TiC, avoiding high concentration of free-C during the phase transformation. A high amount of Ti increase also the fraction of (semi)-coherent TiC in the ferrite phase (most effective for hydrogen trapping). Carbon provides strength and forms the hydrogen trapping system. Depending on the concentration of Ti and on the temperature, the free-C can form cementite (at low temperatures) or TiC (at high temperatures), at which free-C should be avoided. Furthermore, a low level of C and a high level of Ti increase the phase transformation temperature. The higher the transformation temperature, the lower the amount of cementite formed after hot rolling, and the lower the absorbed amount of hydrogen during enamel firing.

But has an impact on mechanical properties through precipitation strengthening

The mechanical characteristics are directly linked to the chemical composition of the steel (solid solution hardening of C and Mn), the ferritic grain size and the quantity and size of the precipitates (precipitation hardening), depending on the processing conditions of the steel (hot rolling, cooling and coiling). As we want to guarantee a minimum level of yield strength after enamel firing, we must take into account that during firing at a temperature above 800°C the material softens, i.e. strength decreases by 35-40%, due to strain relaxation as well as grain and precipitation growth. It is therefore necessary to adjust the chemical composition of the steel so as to obtain this level (S390 level) after enamel firing.

ArcelorMittal now offers S390EK steel grade especially dedicated for silo application

An adapted chemical analysis has been implemented for silo application

Based on the analysis and the constraints mentioned above, ArcelorMittal has developed in its Sestao steel plant a new 2 sides-enamelling hot-rolled steel grade based on a low carbon and high titanium chemistry without the addition of elements such as niobium or vanadium. The idea is to generate enough hydrogen traps through the control of the precipitation of TiC and Ti(C,N) while avoiding the presence of free-C in the steel and, by adapting the manufacturing conditions (hot rolling and coiling temperature), targeting ad-hoc level of mechanical properties to ensure a minimum yield strength of 390 MPa after the enamel firing.

Table 1: targeted chemical composition

Targeted chemical composition (wt %)						
C	Mn	P	S	Si	Al	Ti
≤ 0.07	0.8 – 1.2	≤ 0.025	≤ 0.015	≤ 0.1	0.02 – 0.06	≥ 0.18

The table below shows the results obtained for the mechanical properties before and enamel firing simulation (longitudinal direction and transverse direction).

Table 2: mechanical properties

Direction	Before enamelling			After enamelling			After 2nd enamelling		
	YS (Mpa)	TS (Mpa)	E_{80}%	YS (Mpa)	TS (Mpa)	E_{80}%	YS (Mpa)	TS (Mpa)	E_{80}%
T	≥ 620	≥ 670	≥ 6	≥ 390	≥ 500	≥ 11	≥ 360	≥ 440	≥ 21
L	≥ 600	≥ 650	≥ 8	≥ 380	≥ 480	≥ 12	≥ 340	≥ 430	≥ 24

It is important to note that, to ensure the minimum level of yield strength of 390 MPa after enamel firing, the level of mechanical properties is quite high at material delivery state. We are seeing a loss of about 35% of the yield strength during the enamelling operation. A second firing increases loss of about 10%. However, the use of a S420MC grade will not ensure to guarantee this level of yield strength after firing of the enamel. Indeed the level reached will be about 300 to 350 MPa (considering the same loss percentage).

S390EK steel grade is suitable for two-sides enamelling with the use of current ground enamel

Two sides enamelling ability has been evaluated with the use of fishscale sensitive enamel (Ferro S43) after degreasing and pickling. Enamel firing was carried out between 780°C and 860 °C (use of gradient strips). Targeted enamel thickness: 150 to 200 µm. Enamel adhesion has been tested with current ground enamel used for boiler application. The results are summarised in the following table: a good enamelling ability was obtained in the process window 800 / 840 °C -10 mn (steel thickness = 2 mm)

Table 3: enamelling characterisation

Firing temperature (°C)	Fishscale sensitive enamel (Ferro S43)		Current ground enamel (Pemco PP800/M/62037)	
	Fishscale resistance		Adhesion	Fishscale resistance
	Firing time (mn)		Firing time (mn)	
	8	12	10	10
860	Red	Red	Green	Green
840	Green	Red	Green	Green
820	Green	Yellow	Green	Green
800	Green	Green	Yellow	Green
780	Green	Green	Red	Green

Colour code	Fishscale results	Enamel adhesion
Green	Never fishscales	Very good adhesion (score ≤ 2)
Yellow	Not consistent results	Moderate adhesion (score = 2 – 3)
Red	Always fishscales	Poor adhesion (score ≥ 3)

Figure 3: no fishscale appear on grade S390EK after 2-sided enamelling with sensitive enamel (Ferro S43)

The use of S390EK grade has been validated with 2 coat / 2 fire enamelling process following silo specification (see table 4).

The tests have been carried by Ferro under following conditions:

- 2 coat / 2 fire enamelling process
- Coating thickness: 300 g/m² for each layer
- Firing temperature: 840 °C during 6 mn

Table 4: specification for silo application

Norm	Test	Limits
ISO 28706-1:2008 (§ 9)	Citric Acid – Room temperature	AA
ISO 28706-2:2008 (§ 10)	Hot Citric Acid - 2.5h – liquid phase	0,75 g/m²
ISO 28706-2:2008 (§ 13)	Boiling Water – 48 h – liquid phase	1,5 g/m²
ISO 28706-2:2008 (§ 13)	Boiling Water – 48 h – vapour phase	5,0 g/m²
ISO 28706-4:2008 (§ 9)	Hot soda - 24h	6,0 g/m²
ISO 28706-1:2008 (§ 10)	Sulphuric acid - Room temperature	AA
ISO 28706-1:2008 (§ 11)	Chlorhydric acid - Room temperature	AA
ISO 28706-2:2008 (§ 12)	Hot chlorhydric acid – 7 days – vapour phase	7,0 g/m²
ISO 28706-3:2008 (§ 9)	Detergent Solution - 24h	2,5 g/m²
EN 1388-2: 1996	Cadmium leaching test	<0.05 mg/dm²
EN 1388-2: 1996	Lead leaching test	<0.1 mg/dm²

All the results which were obtained are in accordance with the specification.

The use of new steel grade S390EK leads to substantial savings

We previously reported that the use of steel grade S390EK helps simplify the enamelling process, reduce the rate of repair and so reduce costs. It is no longer necessary to use a sub - layer or enamel highly doped with adhesion oxide. Of course, there is an additional cost required to purchase this grade compared to grade S420MC or equivalent, but it is far outweighed by the savings from the simplification of the process

Furthermore, this steel has a high level of mechanical properties guaranteed after enamel firing. We saw that it was higher than when using a S420MC. Its implementation can reduce the thickness of steel used.

We performed two cost simulations depending on whether the thickness is reduced or not. It is thus clear that significant savings can be achieved with the use of the new grade S390EK.

Table 5: cost simulation without thickness reduction

	Today	Tommorrow
Steel grade	S420MC	S390EK
Thickness (mm)	4,00	4,00
Width (mm)	1420	1420
Yearly consumption (tons)	3000	3000
Steel (€/ton)	592	647
Ground enamel (€/kg)	4,80	2,70
Cover enamel (€/kg)	2,40	2,40
Ground enamel thickness (µm)	300	300
Cover enamel thickness (µm)	100	100
Enamel cost (€/ton of steel)	159	99
Process costs (€/ton of steel)	361	268
Total (€/ton of steel)	1112	1015
Expenses per year (k€)	3336	3044
Your savings per year (k€)		292 8,75%

Table 6: cost simulation considering thickness reduction

	Today	Tommorrow
Steel grade	S420MC	S390EK
Thickness (mm)	6,00	5,00
Width (mm)	1420	1420
Yearly consumption (tons)	3000	2500
Steel (€/ton)	592	647
Ground enamel (€/kg)	4,80	2,70
Cover enamel (€/kg)	2,40	2,40
Ground enamel thickness (µm)	300	300
Cover enamel thickness (µm)	100	100
Enamel cost (€/ton of steel)	106	79
Process costs (€/ton of steel)	241	215
Total (€/ton of steel)	939	941
Expenses per year (k€)	2816	2353
Your savings per year (k€)		463 16,45%

To conclude

Among the materials that can be used for the manufacture of silos and tanks, enamelled steel offers many advantages and is an excellent compromise between cost and sustainability. For this application, it is required to use hot rolled steel having minimum yield strength to withstand the load contained in the silo. Steels used so far are high-strength steels, which are normally not suitable for two-sides enamelling.

Nevertheless, so as to properly enamel these steels on the two sides without risk of fishscales appearance, it is necessary that the enamel adhesion is strengthened, and this is achieved by using sublayers highly doped with adhesion oxides, which have a high cost and present risks with regards to the environment. Indeed, regulations related to REACH and food contact ability may soon limit or ban the use of Ni or Co metallic oxides required to improve enamel adhesion on steel. Therefore, ArcelorMittal has developed a new high strength steel grade, called S390EK, especially dedicated for 2 sides enamelling purpose (1C/1F, 2C/1F or 2C/2F), without requiring any special surface treatment or the use of doped sub layers or ground enamels, with guarantee against fishscaling and presenting a minimum level of yield strength of 390 MPa after enamel firing. The implementation of this steel allows enameling panels under environmental friendly conditions while saving money on manufacturing costs.

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