

Dalnox Bright™: new annealing and pickling line process technology for cold-rolled stainless steel strip

Dalnox Bright™ process technology combines the high productivity of conventional annealing and pickling lines with a high surface quality, reduced cost and the added advantage of an environmentally friendly process.

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Currently, cold-rolled stainless steel strip is generally supplied in two surface finishes according to EN10088/2:

- 2D/2B cold rolled, annealed, pickled and skin passed (2B)
- 2R cold rolled, bright annealed (BA) and skin passed

2D/2B surface finish is generally produced on horizontal high-capacity continuous annealing and pickling lines (A&PL), with a productivity of up to 150t/hr, in which the strip is annealed in an oxidising atmosphere (combustion gas mixture). The oxide layer produced during annealing has to be removed and then passivity has to be restored. This is generally achieved by an electrolytic descaling process followed by a chemical pickling treatment, usually using mixed acid (HNO₃/HF). Large amounts of polluting substances, such as NO_x emissions, nitrates in the disposal water and sludge, are produced that require special treatment processes.

2R surface finish is obtained on vertical bright annealing plants in which the strip is annealed in an H₂/N₂ gas mixture with a controlled dew-point, preventing surface oxidation. Consequently, pickling processes are not required. The vertical furnace orientation, however, reduces the productivity, presently limited to a maximum of approximately 20-25t/hr. Due to their mirror properties and good appearance, 2R surface finish products are generally preferred to 2D/B for so-called 'on-sight applications'.

By combining the main, positive features of both of these methods, an innovative process technology called Dalnox Bright™ has been developed for annealing and pickling of cold-rolled stainless steel strip.

PROCESS AND TECHNOLOGY

Worldwide market globalisation is driving steelmakers to research new processes and technologies that can reduce

production costs and increase competitiveness, and improve steel quality while reducing the environmental impact of the production processes. In pursuing such targets, Danieli and Centro Sviluppo Materiali (CSM) have developed Dalnox Bright™, a process that produces stainless steel strips with an enhanced surface quality, close to 2R, and plants with the same production capacity and cost of conventional A&PLs. An expected benefit is a decrease in the environmental impact of chemical pickling processes.

The key aspect of the technology is a dramatic reduction in oxidation during annealing compared with conventional A&PLs. As a consequence, chemical pickling treatment is eliminated or reduced, which results in enhanced surface quality, savings in pickling treatment and a reduction in the volume of waste solution to be neutralised.

Control of the oxide film formation is achieved by using specific strip thermal cycles and close control of the oxidising capability of the annealing atmospheres at each processing step (heating and cooling), with particular attention to the higher temperature ones.

The fundamental steps of the process technology are:

- A rapid heating stage in a controlled oxidising atmosphere in which oxide nucleation and thin oxide film formation occur
- An annealing stage to complete metallurgical transformation (to obtain required mechanical properties, grain size, carbide solubilisation, etc), in a non-oxidising atmosphere (N₂) in order to limit oxide layer growth
- A cooling stage in a non-oxidising atmosphere at cooling rates able to avoid carbide precipitation
- An efficient electrolytic descaling stage
- A light chemical pickling stage with reduced environmental impact and surface passivation. For the best surface finish, this step can be avoided

RESEARCH AND DEVELOPMENT

Dalnox Bright™ was first developed at CSM's laboratory facilities, using existing know-how in continuous annealing and pickling continuous processes and plants for stainless steel strip. Later, the new process was tested on the continuous annealing pilot plant in Danieli's R&D department. Surface characterisation and pickling tests of annealed samples were performed.

ANNEALING

The oxidation phenomena occurring on AISI 304 stainless steel strip for both conventional and Dalnox Bright™ annealing processes are illustrated in *Figure 1*. In the Dalnox Bright™ initial heating stage for annealing (up to 850-950°C), oxidation is reduced by the formation of a protective thin oxide layer in a controlled atmosphere at higher heating rates than conventional ones. During annealing at the higher temperature range where major oxidation normally occurs, the presence of a non-oxidising atmosphere guarantees limited oxide build-up. Then, during cooling the presence of non-oxidising conditions prevents further oxide growth. *Figure 2* shows the mean oxide film thickness present on AISI 304 annealed strip produced with conventional and with Dalnox Bright™ processes.

PICKLING

In conventional cold-rolled A&PLs the pickling section is generally sub-divided into two parts: an electrolytic section (generally neutral Na₂SO₄ bath) which dissolves the oxide layer, and a chemical section (mixed acid HNO₃/HF baths or ecological baths) which removes residual scale by dissolving the reactive layer underneath and restores passivity.

Due to the reduced oxidation using Dalnox Bright™, the thin oxide layer is easily removed by a simple electrolytic descaling treatment in a conventional electrolytic section. After electrolytic treatment, the strip surface appears free from oxide with a surface finish (in terms of mirror properties) close to 2R. The histograms in *Figure 3* show the gloss measurements (60°) of samples obtained with Dalnox Bright™ after electrolytic descaling, compared with those of standard 2B and 2R surfaces. The short strokes added on top of the gloss bars indicate the increase in gloss normally obtained after skin passing.

The final light chemical treatment (low temperature, low HF content, shorter treatment time) ensures complete pickling even under A&PL non-standard working conditions (eg, furnace transitory due to both productivity and material changes, line slow-down). Due to the dramatic reduction in oxidation, which in turn strongly decreases the steel surface reactivity, the final light chemical pickling is characterised by reduced specific mass loss and pickling

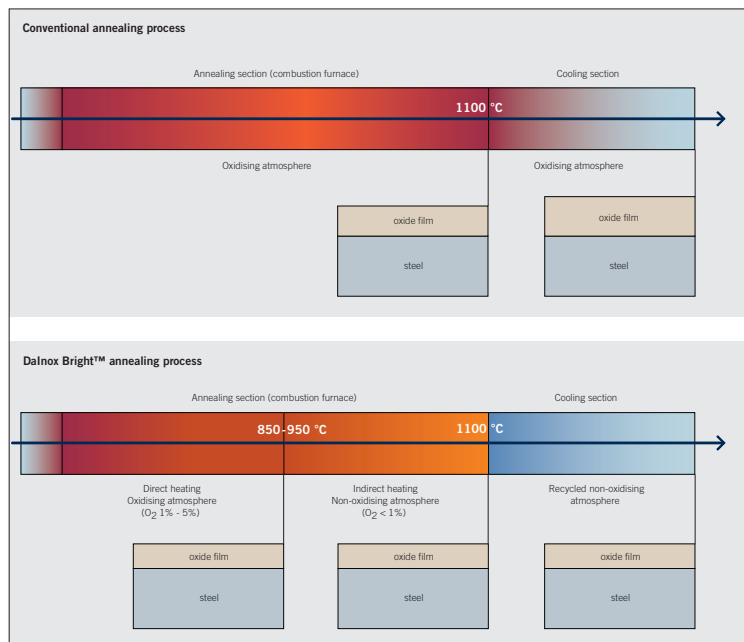


Fig 1 Oxidation phenomena in conventional and Dalnox Bright™ annealing processes

times, compared to conventional processes. *Figure 4* shows the specific percentage mass loss in mixed acid chemical pickling (HNO₃/HF) compared to that observed on standard annealed products (2D).

PILOT PLANT

The annealing pilot line installed at Danieli R&D can continuously treat 0.4-2.0mm thick and 300mm wide steel strips at a speed of up to 10 m/min. Its modular design means it can reproduce different annealing cycles and furnace atmospheres (see *Figures 5a and b*). It is made with refractory materials that allow temperatures of up to 1,400°C to be reached in the heating zones, and is equipped with process control instrumentation. The second zone of the furnace, where the strip reaches the maximum temperature, is heated indirectly by either electrical resistance heaters or flame burners. Many experimental campaigns were devoted to the definition of the best process conditions, and scaling-up criteria and related industrial technologies have been defined.

FIELD OF APPLICATION

It is possible to obtain surface quality close to BA and standard 2D/2B on all stainless steel grades (austenitic, ferritic and duplex) using this technology. Only about 20% of total energy transferred to the strip in the annealing process is supplied by indirect heating systems such as electrical resistances or radiant tubes.

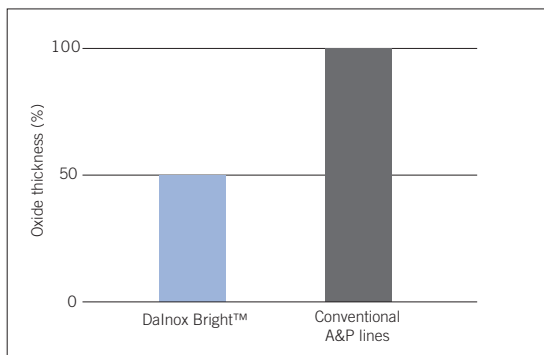


Fig 2 Comparison of mean oxide film thickness on AISI 304 annealed strip

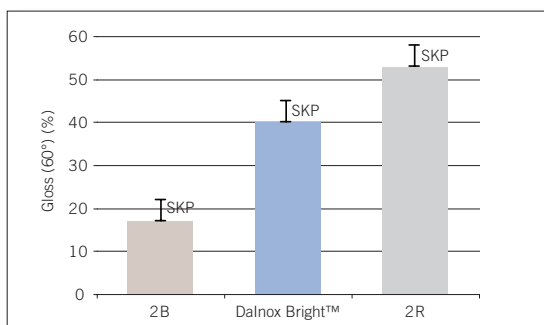


Fig 3 Comparison of gloss measurements (60°)

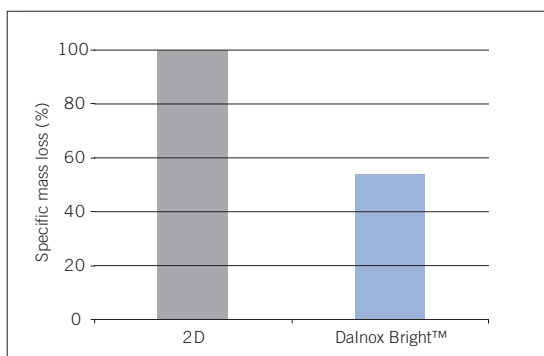


Fig 4 Comparison of specific mass loss in mixed acid pickling

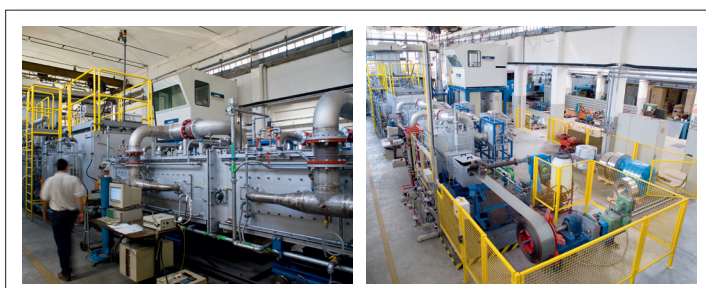


Fig 5a 5b Dalnox Bright™ annealing pilot plant

COST EVALUATION

A cost analysis based on average Italian energy and material market prices has been performed, taking into account the following operating charges:

- Energy (fuel gas) and process gas consumption in the annealing section
- Electrical energy and chemical consumption in both electrolytic and chemical pickling sections
- Neutralisation and disposal of waste solutions and fumes
- Human resources directly involved in plant operations
- Metal loss (yield) due to annealing and pickling treatment

Using the above the operating costs of Dalnox Bright™ A&PL is ~35–40% lower than for conventional A&PL ones (AISI 304).

SUMMARY

The main advantages of Dalnox Bright™ process technology are:

- Same productivity as conventional A&PL
- High flexibility in terms of surface appearance of the 2D product or close to a 2R finish
- Reduced or eliminated chemical pickling with consequent savings on equipment and management costs
- Reduced environmental impact and savings on emissions and waste neutralisation treatment costs
- Enhanced surface quality
- Suitable for both new and existing plants. In the case of existing plant, the upgrading of the furnace, without any changes on the pickling section, could give a profitable increase in productivity, thanks to decrease in the strip oxidation. **MS**

Dalnox Bright™ is a patented process technology and a Danieli trademark.

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