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Surface composition of heat-treated steel sheets*

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The chemistry of the surface of temper-rolled strip results from different interactions taking place at each step of the cold-processing line. For example, after descaling, pickling oil is applied to the strip to ensure a protective coating and to provide a lubricant for the cold-reduction step. For cold-rolling, an emulsion of oil in water is used to help lubrication and heat dissipation. Such treatments, involving the use of different chemical agents such as pickling acid, industrial water, corrosion inhibitors and mixtures of fats, fatty acids and bactericides result in contamination of the external layers of the steel strip.

In order to allow high cold reduction rates, needed for black-plate rolling, a lubricant is used containing palm oil or a blend of tallows in a water-based emulsion, which cannot be removed by distillation during batch annealing but can be easily saponified by electrolytic alkaline cleaning. For such a product, a so-called 'clean surface' is obtained by this degreasing treatment. During the subsequent annealing treatment, many physico-chemical reactions such as diffusion or oxidation may occur, resulting in chemical enrichment of the external surface.

Experience to date shows that graphite formation occurring on the external surface cannot be related to residues of oil emulsion but is due to carbon migration from the bulk to the external surface. Such graphite formation on the batch annealed black-plate surface cannot be removed by any chemical treatment normally used in a tinning line and results in a 'frosty tinplate' (Inokuti 1975; Hunter & Baird-Kerr 1974).

The main purpose of our work is to define the surface composition of the steel strip respectively after degreasing or batch-annealing. In order to define the surface compositions, specimens were taken from industrial lines at different steps of the processing line, and examined by surface analytical techniques such as the secondary ion mass spectrometry (s.i.m.s.) with imaging facilities, Auger electron spectrometry (A.e.s.) and X-ray photoelectron spectrometry (X.p.s.). The results may be summarized as follows.

As a consequence of the alkaline degreasing treatment, a silica film, $\text{Si}(\text{OH})_4 \cdot n \text{H}_2\text{O}$, is formed on the external surface by gelation of the orthosilicic acid during rinsing at pH 7. The thickness of this film ranges from 2 to 4 nm and depends on the hardness, and more precisely the calcium content, of the water used in degreasing and rinsing solutions.

The batch-annealing treatment induces some interactions between the silica film and the steel substrate which result in segregation of elements such as Mn, Cr, and P. Owing to the oxygen potential resulting from the silica film, oxidation of these elements occurs at the free surface or in the grain boundaries. The thickness of the oxide layer is normally in the range 5–8 nm. Graphite formation on the external surface due to cementite destabilization and carbon migration during batch annealing is strongly reduced by the presence of the silica film. The efficiency of this inhibition is improved by the addition of sulphur bearing compounds in the rinsing bath of the degreasing treatment (Pemvalt Co. Patent no. 3,632,487).

* Extended abstract.

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Finally, it should be mentioned here that such a real surface may be considered as a clean surface and is perfectly adequate, for example, for a bright tinning.

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