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Paton Ron Wilson
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THE EFFECT OF MANGANESE AND CHROMIUM ON THE
SELECTIVE OXIDATION OF LOW CARBON STRIP
STEELS FOR TINPLATE APPLICATIONS

**A thesis submitted in fulfilment of the
requirements for the award of the degree**

DOCTOR OF PHILOSOPHY

from

UNIVERSITY OF WOLLONGONG

by

PATON RON WILSON

Faculty of Engineering

2006

**I, Paton Wilson, hereby certify that the work embodied in this
thesis is the result of original research and has not been submitted
for a higher degree to any other University or Institution.**

Paton Wilson

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Abstract

The ‘edge defect’ is a band of low reflectivity that occurs near the edge of batch annealed steels that have been tinplate. The tinplate product that contains this defect must be scrapped because of the poor aesthetical properties and the reduced corrosion resistance in the affected areas. This defect was known to be caused by surface precipitates formed during batch annealing of the steel strip substrate. This research aims to identify the surface precipitates and the factors that can be modified to reduce their formation in an effort to develop an alloying and/or processing strategy which eliminates the occurrence of the ‘edge defect’.

In this investigation the ‘edge defect’ was characterised using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) which demonstrated that surface MnCr_2O_4 spinel precipitates were responsible for the ‘edge defect’ although two different oxides, $(\text{MnFe})\text{O}$ and MnCr_2O_4 spinel, were observed on the steel surface. The formation of the surface $(\text{MnFe})\text{O}$ and MnCr_2O_4 spinel was due to the selective oxidation of manganese and chromium during batch annealing. The effects of manganese, chromium and annealing temperature on selective oxidation were also investigated and it was found that the MnCr_2O_4 spinel precipitate size and distribution were directly affected by the content of the chromium in the steels. The higher the chromium content of the steel the coarser the surface MnCr_2O_4 spinel particles. The annealing temperature has a similar effect on the average size of the MnCr_2O_4 spinel. Within the range of this investigation the higher the annealing temperature the coarser the surface particle size.

The surface precipitates across the width of industrial batch annealed steel strip were characterised using SEM and TEM which established that the diameter of the surface oxide precipitates decreased from the edge to the centre of the steel strip. However, for the steel strip which exhibits the ‘edge defect’ the maximum size of the surface precipitates does not occur at the edge, rather about 20-100 mm from the edge. This has been interpreted as the result of the transition of internal selective oxidation to external selective oxidation suggesting that the steel sheet’s exhibiting the ‘edge defect’ are exposed to relatively higher oxygen potentials.

This investigation has identified that lowering the annealing temperature, reducing the chromium level in the steel and reducing the oxygen potential of the annealing environment will reduce the formation of the MnCr_2O_4 spinel. Therefore the 'edge defect' may be reduced by modifying these parameters during tinsplate production. The minimisation of this defect will reduce production costs and improve product consistency for tinsplate production.

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List of Abbreviations

AES	Auger Electron Spectroscopy
BCC	Body Centred Cubic
EDS	Energy Dispersive X-Ray Spectroscopy
FCC	Face Centred Cubic
FIB	Focussed Ion Beam Miller
GDOES	Glow Discharge Optical Emission Spectroscopy
LHS	Left Hand Side
RHEED	Reflection High-Energy Electron Diffraction
RHS	Right Hand Side
SEM	Scanning Electron Microscopy
SIMS	Secondary Ion Mass Spectrometry
SNMS	Secondary Neutrals Mass Spectrometry
TEM	Transmission Electron Microscopy
XPS	X-Ray (excited)-Photoelectron Spectrometry
XRD	X-Ray Diffraction