The Influence of Rolling Oil Decomposition Deposits on the Quality of 55Al-43.4Zn-1.6Si Alloy Coatings

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Table of Contents

Chapter 2 - Experimental

Chapter 4 - Impact of Sulfur and Phosphorus Lubrication Additives and their Thermal Decomposition Products on 55Al-43.4Zn-1.6Si Metallic Coating Quality

Chapter 5 - Impact of Substrate and Furnace Atmosphere Composition on the Decomposition of a Commercial Cold Rolling Oil

Chapter 6 - Development of a Thermal Analysis Test for Predicting Rolling Oil Performance With Respect to Metallic Coating Quality

Summary

Uncoated defects in hot dip metal-coated steel products result from non-wetting of the steel surface by the molten alloy. The occurrence of uncoated defects is highly detrimental to product quality and production efficiency; uncoated defects compromise the appearance and anti-corrosion performance of hot dip metal-coated steel products and causes time delays in the application of subsequent surface treatments. Although many studies have been directed towards evaluating the effect of steel pre-heat temperature and oxidation on the formation of uncoated defects, fewer investigations have analysed how oil-derived residues remaining on steel surface following the cold rolling and furnace cleaning processes impact upon hot dip metallic coating quality. Furthermore, although a considerable amount of research has focussed on the process of deposit formation in lubricants used in other applications, the composition of oily residues remaining after the continuous annealing process, and the origins of these residues in the original rolling oil formulation, are poorly understood.

The primary focus of the present work has been to gain an improved understanding of relationships between cold rolling oil composition, oil residue-formation characteristics and the occurrence of uncoated defects in 55Al-43.4Zn-1.6Si hot dip metallic coatings. Several key classes of rolling oil ingredients which decompose to leave high levels of thermally-stable residue have been identified. The thermal decomposition processes undergone by a variety ingredients within these classes have been studied under both oxidising and reducing conditions using Thermogravimetric Analysis (TGA) and Pressure Differential Scanning Calorimetry (PDSC) techniques, with chemical characterisation of the decomposition process and the resultant thermally-stable residue by infrared spectroscopy. Model blends of each ingredient in a typical cold rolling oil base ester have also been evaluated by TGA and PDSC to identify the impact of ingredient concentration and chemical structure on the amount of oily residue formed. The results of these investigations have been related to the impact of the ingredients on

55Al-43.4Zn-1.6Si hot dip metallic coating quality through the performance of industrial-scale hot dipping trials and hot dip simulation studies.

In order to translate these results into a context more closely aligned with industrial conditions, the effect of processing variables, including furnace atmosphere and the availability/concentration of iron in contact with the rolling oil at the steel surface, on the decomposition process of a fully-formulated commercial cold rolling oil has also been investigated. The information gained can potentially be used to tailor operating conditions within the cold rolling/continuous hot dip metallic coating processes to enhance steel surface cleanliness.

Finally, the deposit-forming tendencies of an array of different commercial cold rolling oils have been evaluated, leading to the development of a thermal analysis-based test for screening cold rolling oils with respect to their likely impact upon 55Al-43.4Zn-1.6Si hot dip metallic coating quality. This test, together with the understanding obtained on the effect of different rolling oil ingredients on hot dip metallic coating quality, can be used within the industry to formulate improved cold rolling oils.

'I certify that this thesis does not incorporate without acknowledgement any material previously submitted for a degree or diploma in any university; and that to the best of my knowledge and belief it does not contain any material previously published or written by another person except where due reference is made in the text.'

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(R.J. PILLAR)

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List of Figures

Chapter 1

Chapter 2

Chapter 3

Chapter 4

Chapter 5

Chapter 6

List of Schemes

Chapter 1

Chapter 3

Chapter 4

Chapter 5

List of Tables

Chapter 1

Chapter 2

Chapter 3

Chapter 4

Chapter 5

Chapter 6

Glossary

Abbreviations

55Al-43.4Zn-1.6Si	alloy containing 55 % w/w aluminium, 43.4 % w/w zinc and 1.6 % w/w silicon
ATR	Attenuated Total Reflectance
AW	Anti-Wear
CI	Comprehensive Index for evaluating rolling oil performance with respect to metallic coating quality
CRM	Cold Rolling Mill
DAPS	di-alkyl pentasulfide
DFF	Direct Fired Furnace
DSC	Differential Scanning Calorimetry
DTG curve	curve obtained by plotting the first derivative of mass loss with respect to temperature
E_a	activation energy
EDS	Energy Dispersive Spectroscopy
EP	Extreme Pressure
FFA	Free Fatty Acid
FTIR	Fourier Transform Infrared Spectroscopy
HNX	5 % hydrogen-95 % nitrogen gas mixture
LSCM	Laser Scanning Confocal Microscopy
MCL3	hot dip metallic coating line no. 3 at BlueScope Steel®'s Port Kembla Works
MTGA	Modulated Thermogravimetric Analysis; Modulated Thermogravimetry
NMR	Nuclear Magnetic Resonance
PI	Index calculated from PDSC parameters for evaluating rolling oil performance with respect to metallic coating quality

PDSC	Pressure Differential Scanning Calorimetry
RF	Reduction Furnace
SEM	Scanning Electron Microscopy
SLO	Sulfurised Lard Oil
SVO	Sulfurised Vegetable Oil
T_{end}	decomposition end temperature; the temperature within the range of analysis after which no further heat flow/mass loss events are observed
TG curve	curve obtained by plotting mass loss with respect to temperature
TGA	Thermogravimetric Analysis
TI	Index calculated from TGA parameters for evaluating rolling oil performance with respect to metallic coating quality
ToF-SIMS	Time-of-Flight Secondary Ion Mass Spectrometry
T_{onset}	onset temperature of mass loss or oxidation (as specified)
T_{max}	maximum rate of mass loss or maximum heat flow temperature (as specified)
TPS 20	di-*tert*-dodecyl trisulfide
RF	Reduction Furnace
XR81627, XR81628, XR81629, BSLWP1.1, 560453, 560350, 560350noS, U1388501, SB4198, CAT29, N609DPD, XR82154	names of commercial cold rolling oil formulations

Terminology

The terminology outlined below is used to describe rolling oil/rolling oil ingredient decomposition processes throughout this work.

Decomposition step. Any process for which the rate of mass loss (TGA) or the heat flow (PDSC) does not go through zero is considered to be a single step process for the purposes of kinetic evaluation. Therefore, the term 'decomposition step' will be used to refer to sections of the decomposition process that are bounded by the rate of mass loss/heat flow passing through zero. For the majority of oils/oil ingredients analysed in this research, the decomposition process never passes through zero and therefore occurs via a single decomposition step.

Decomposition event. The term 'decomposition event' is used to refer to a decomposition process that is not bounded by the rate of mass loss (TGA) or heat flow (PDSC) passing through zero. Decomposition events are identifiable by a change in the rate of mass loss/heat flow and may appear as 'peaks' or 'shoulders'.

Decomposition region. For the majority of oils/oil ingredients studied, it was possible to group decomposition events two well-defined temperature regions. These regions are denoted as the primary (A) decomposition region, which includes decomposition events occurring between room temperature and 300 ^{o}C, and the secondary (B) decomposition region, which includes decomposition events occurring between 300-500 ^{o}C (note that fin Chapter 3.1, different temperature ranges are used). The % B/A ratio, used to indicate the residue-forming tendency of an oil, can be determined from the ratio between the amount of mass loss (TGA) or heat flow occurring over the secondary and primary decomposition regions.