

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

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Thesis submitted to the Faculty of Science and Engineering  
of Flinders University  
in fulfilment of the requirements  
for the degree of

**DOCTOR OF PHILOSOPHY**  
in  
**CHEMISTRY**

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ADELAIDE  
AUSTRALIA

September 2007  
Adelaide, South Australia

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# 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.'

.....

(R.J. PILLAR)

# Acknowledgements

Before I thank the individuals who have helped me along the road to achieving my goals, I would like to thank:

- the two Universities at which I have studied, Flinders University and the University of Wollongong;
- the Australian Research Council (ARC), for funding this research through its Linkage Grant scheme, and
- BlueScope Steel<sup>®</sup> and Quaker Chemical, for their financial and considerable in-kind contributions.

The first thing that must be said about working on this research project is that it has been one of the most rewarding experiences of my life. It has given me the opportunity to travel and meet so many wonderful people who, together with my friends and family, have all enriched my life and provided me with much-appreciated support over the past four years. For this they deserve the following acknowledgement.

From Flinders University, I wish to express my most heart-felt gratitude to Dr Milena Ginic-Markovic, who has mentored me through the good and the bad, been a wonderful friend and colleague and who has showed extreme strength of character and tenacity in proof-reading this thesis for me! I would also like to thank my supervisors, Prof Janis Matisons and Dr Stephen Clarke, for always encouraging me and for providing me with so many wonderful opportunities. To the mechanical and electrical ‘workshop guys’ at Flinders University I offer my most earnest thanks; no broken piece of equipment or urgent request was ever too much trouble! I would especially like to acknowledge Mr Mike Mellow for his patience and assistance in helping me to install the TGA and PDSC at the commencement of my PhD. Thank-you to all who have worked as part of the Matisons/Clarke research groups for your camaraderie, especially Ms Tricia Butterfield for everything she has done on both a personal and professional level and Dr Kristina Constantopoulos for sharing an enduring friendship and for motivating me to achieve my best (the ‘Dr’ still makes me smile).

From the University of Wollongong I would like to thank my supervisor, Prof Hugh Brown, for helping to make my brain tick over on both research-related and ‘life’ issues. I also appreciate the wonderful, kind support of Prof Rian Dippenaar. Without the help of Dr Dominic Phelan and Mr Mark Reid I would have never understood half as much metallurgy or had half so much fun. I would also like to express my appreciation towards Mr Greg Tillman, Mr Bob De Jong and Mr Nick Mackay for their technical assistance. Thanks to Dr Chris Lukey and Dr Sandra Cram for their professional support and friendship and thanks to everyone in the old ‘BHP Steel Institute’ student office and the wonderful people who went to the Uni Bar with me on Friday afternoons! When I first arrived in Wollongong my flatmate, Ms Katarina Nordmark, immediately took me ‘under her wing’ and I would like to acknowledge her beautiful friendship, faith and support. I would also like to give my special thanks to my second Wollongong flatmate, the new ‘Doctora’ Wanda Melfo, for having such a positive influence on my life.

Whilst working on this project, not only did I have the support of supervisors from the two Universities; I was lucky enough to have industrial supervisors from both BlueScope Steel® and Quaker Chemical: Dr David Willis, Mr Wayne Renshaw, Mr Warren Bell and Mr Andrew Gibson. These people deserve every thanks I can offer them they have invested so much of their time in me and showed such a keen interest in my research that they made working on this project immensely rewarding and enjoyable. I also wish to acknowledge others from BlueScope Steel® and Quaker Chemical who have helped me along the road to completing my research, in particular:

- Ms Bridget Newman and Mr Kevin Podolski, for helping me undertake industrial hot dipping trials;
- Dr Daniel Yuen, for collecting steel samples and providing me with valuable feedback;
- Dr Qiyang Liu and Dr Joe Williams for their assistance with performing hot dipping simulations;
- Dr Rex Chen, for his guidance and interest in my research, and
- Dr Peter Schellingerhout, for his wonderful support and for asking the hard questions!

My appreciation and thanks also go to Dr Grant van Riessen from LaTrobe University for analysing my samples by ToF-SIMS.

To my life-long friends, Kate Wycherley, Brenda Woods, Jess Smith and Leanne Pridham, thank-you so much for your support and friendship. I'm so glad that we can finally share that long lunch/beer/coffee I've been hanging out for!

Last and by every means most importantly, thanks go to my family for everything they have taught me and for the dedicated love and support they have provided. To my parents, Janet and Graham Pillar, to my sister, Lauren Pillar, and to my grandparents, Jean and Dennis Arrowsmith, thank-you. I will always remember, Grandad, that a trouble shared is a trouble halved. I would also like to thank Ann and Wren Lashmar and 'Nanna' Miri Dalton for their kindness, love and unwavering support over the past four years and beyond. Lastly, to my incredible boyfriend, Kym Lashmar, for loving me, for knowing and understanding my quirks and for providing a serene balance to my life – thank-you.



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# 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
DFE	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 <sup>®</sup> '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 <sub>end</sub>	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 <sub>onset</sub>	onset temperature of mass loss or oxidation (as specified)
T <sub>max</sub>	maximum rate of mass loss or maximum heat flow temperature (as specified)
TPS 20	di- <i>tert</i> -dodecyl trisulfide
RF	Reduction Furnace
XR81627	names of commercial cold rolling oil formulations
XR81628	
XR81629	
BSLWP1.1	
560453	
560350	
560350noS	
U1388501	
SB4198	
CAT29	
N609DPD	
XR82154	



## **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 °C, and the secondary (B) decomposition region, which includes decomposition events occurring between 300-500 °C (note that in 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.