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Bao Jiang Xu
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Xu, Bao J, Nucleation and growth of 55 percent Al-Zn alloy on steel substrate, PhD thesis, Faculty of Engineering, University of Wollongong, 2005. <http://ro.uow.edu.au/theses/72>

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Nucleation and growth of 55% Al-Zn alloy on steel substrate

**A thesis submitted for
the degree of**

**Doctor of Philosophy
By**

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May 2005

*I 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 University or Institution*

ABSTRACT

The nature of nucleation and growth of the alloy overlay of a 55% Al-Zn alloy on a steel substrate strongly affects the surface appearance of hot dip metal-coated steel in the Zinalume process. The potential nucleation site of the first nucleus that forms in the alloy overlay will contribute to the initial solidification process and subsequent microstructural development. An important issue of industrial interest is the occurrence of localized variations in spangle size or variations in spangle size from coil to coil. Control of spangle size on hot-dip metallic coatings is important both from an aesthetic and functional point of view. From the point of view of surface appearance, a uniform spangle size is required and small spangle size is required for improvement of tension bend rust stain performance. An attempt was made to reveal the nature of nucleation and growth of the Al-Zn overlay by studying early stage nucleation and growth. The effect of cooling rate on spangle formation, the influence of trace element additions, the effects of dipping time, preheat temperature and bath composition were taken into account during experimental immersion tests. Spangle size, dendrite arm spacing and solidification temperature of the alloy overlay were determined under various cooling conditions and a variety of other techniques were used to analyze the progress of solidification.

Experiments were conducted in the current study to determine the influence of process variables on spangle size. An experimental immersion simulator was used to test the hypothesis regarding nucleation on intermetallic particles using a quench- interruption technique. Serial sectioning in combination with microprobe studies has been used to

quantify the element distribution. Commercial products have been analyzed using a tilt polishing technique combined with EPMA to assess element distribution across the solidified overlay. Also, bulk analysis of the element distribution through the thickness of commercial products has been conducted using Glow Discharge Spectroscopy. These experimental studies provided convincing experimental evidence that 55%Al-Zn spangles nucleate on the intermetallic layer. In an attempt to verify that the experimental observations are scientifically founded, a model was developed to predict the nucleation rate and nucleation temperature. Thermodynamic analyses as well as phase-field modeling have been used to further correlate the experimental findings with theoretical predictions. The rate of nucleation decreases with an increase in wetting angle, and the nucleation temperature decreases with increasing cooling rate. Phase-field modeling predicts that an aluminum rich phase forms at the intermetallic layer, acting as the nucleus of a spangle.

Experimental studies on spangle size distribution of 55%Al-Zn have indicated that the cooling rate and bath composition are factors that influence spangle size. An attempt to prove that experimental observations are scientifically forwarded, modeling of nucleation rate, nucleation temperature, thermodynamic analysis as well as phase-field modeling have been conducted. An advantage of the modelling techniques is that the rate of nucleation and nucleation temperature as function of undercooling and cooling rate can be extrapolated beyond the experimental findings. A description of heterogeneous nucleation was modeled to elucidate the effect of cooling rate on the rate of nucleation and nucleation temperature, The rate of nucleation decreases with an increase of wetting angle, and the nucleation temperature decreases with increasing the

cooling rate, also the microstructural evolution at different nucleation sites during solidification of 55%Al-Zn coating is simulated using a phase-field model, A comparison of this experimental observation with the phase field simulations reveals good correlation with the case where dendrite growth was initiated at the intermetallic layer. Detail examination and thermodynamic analysis explained the occurrence of the different intermetallic phases on the alloy layer that could provide potent nucleation sites and hence lead to variation of spangle size.

Consideration of nature of nucleation and growth of 55%Al-Zn alloy on steel substrate was taken to clarify the variation of spangle size. In combination with modified immersion simulator and various measuring techniques and modeling approaches, it concluded that the intermetallic layer is potent nucleation site and results in spangle size variation, also the cooling rate and trace elements play role in the spangle size.

ACKNOWLEDGEMENTS

I am privileged to have had Prof. Rian Dippenaar, Dr Dominic Phelan as my supervisors and my deepest gratitude goes to them for their guidance and encouragement. In particular, many thanks go to Prof. Rian Dippenaar for his direction, passion for science and his careful check and revision on the thesis. Also many thanks go to Dr. Dominic Phelan for many detailed technical discussions during the course of this study.

I express my sincere thanks to my industrial supervisor Dr. David Willis at Bluescope Research Laboratory. His rich knowledge, and scientific attitude has had a significant influence on this study. Also thanks go to Bluescope staff, Mr. Les Moore for EPMA analysis, Dr. Qiyang Liu for the hot dipper experiments, Dr, Damien Jinks, Ms Adonia McCulloch for GDS analysis and Mr. Bob de Jong for designing the quench rigs and technical staffs in metallographic Laboratory

Thanks go to the Australian Research Council and Bluescope Steel Ltd for funding the project. I also express thanks to staff and postgraduates at Bluescope Steel Institute.

To my family, thank you for your love, patience, understanding and support.

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Nomenclature

A	Surface or cross-sectional area	m^2
c_R	Equilibrium solute concentration for a interface of radius R .	kg m^{-3}
C_p^l	Heat capacity	J/mol K
D_i	Diffusion coefficient of the solute	m^2/s
E	Internal energy of the phase	J
G_L	Gibbs free energy of the liquid	J/mol
G_s	Free energy of the solid	J/mol
H_L	Enthalpy at liquid state	J/mol
H_E	Enthalpy at solid state	J/mol
h	Convective coefficient	$\text{W/m}^2 \text{K}$
k	Thermal conductivity	W/Km
k_B	Boltzmann's constant	J/K
k_s	Kinetic parameter for surface nucleation	N/m^{-2}
L	Difference of enthalpy	J/mol
n^*	Steady state population of critical nuclei	Nuclei/m^{-3}
m_{ik}	Linear coefficient of deviation from thermodynamic equilibrium	-
n	Number of nuclei	-
N_A	Avogadro's number	-
N	Number (atom of liquid)	-
I	Nucleation rate	$/\text{m}^3 \text{s}$
I_s	Surface nucleation frequency	$\text{m}^{-2} \text{s}^{-1}$
P	Perimeter of the volume element	m
P	Pressure	Pa
Q	Activation energy	J/mol
r^*	Critical nucleus radius	m

R	Curvature of interface	m
S	Entropy J/mol	K
T	Absolute temperature	K
T_r	Dimensionless temperature	-
T_l	Liquidus temperature	K
\dot{T}	Cooling rate	K/s
T_N	Nucleation temperature	K
T_E	Environment temperature	K
T_{rg}	Reduced glass transition temperature	K
T_0	Initial temperature of the steel strip	K
T_e	Solidification temperature	K
V	Volume	m ³
V	Atomic value	m ³
α	Dimensionless liquid/solid interface energy parameter	-
β	Dimensionless entropy of solidification	-
β	The rate at which critical nuclei become stable due to the addition of more atoms	s ⁻¹
ε_{ik}	Defined as the gradient energy coefficient of phases i and k	-
ϕ	State of the phase	
ω	A factor which include the vibration frequency of the atoms and the area to which atoms can join critical nucleation	s ⁻
η	Viscosity of the liquid	Nsm ⁻²
η	Interface thickness	m
θ	Wetting angle at the equilibrium configuration.	degree
ρ	Density of alloy	kg/mm ²
σ	Surface tension	N/m
σ	Solid/ liquid interface energy	J/m ²
σ_{sv}	Interfacial energy of the solid/vapour	N/m
σ_{sl}	Interfacial energy of the solid/liquid	N/m

σ_{ij}	Interfacial energy of phases i and j	N/m
Δg	Gibbs free energy per unit volume	J/m ³
ΔG_i	Surface free energy	J/mol
ΔG_v	Volume free energy	J/mol
ΔG	Gibbs free energy for this critical size	J/mol
ΔG^*	Standard free energy	J/mol
ΔS	Change of entropy	J/mol
ΔS_{ij}	Entropy of fusion of phases i and j	J/mol
\hat{f}	Free energy of system	J/mol
ϕ_i	Order parameter for each phase or grain	-
ε_{ik}	Gradient energy coefficient of phase i and k	-
m_{ik}	Linear coefficient of deviation from thermodynamic equilibrium	-
ΔS_{ij}	Entropy of fusion	J/mol
ΔT_{ij}	Equilibrium undercooling	K