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**SURFACE PROPERTIES AND FINISHING
OF ALUMINIUM CASTING ALLOYS**

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A thesis submitted in fulfilment of the requirements for
the degree of Doctor of Philosophy in Chemistry (Materials Science)

The University of Auckland, 2009

ABSTRACT

Aluminium alloys are materials of huge practical importance. However their use is dependent on surface oxides and hydroxides which are critical in protecting the highly reactive underlying metal. The stability and integrity of the oxides and hydroxides are also crucial in finishing and bonding applications. Better understanding of these surfaces has significant implications in enhancing their application.

LM6 and LM25 aluminium-silicon casting alloys were studied as these materials show a particularly inhomogeneous phase structure and complex surface behaviour. This complexity is of fundamental interest and leads to considerable practical difficulties, especially in surface finishing. The surfaces were characterised, subjected to thermal treatments and modified with Ion Assisted Deposition coatings of TiN. A characterisation method for these surfaces was also developed based around the layered structure of aluminium hydroxides.

It was observed that the thermally induced surface segregation of minor elements, such as Mg and Na, is availability-limited. Surface concentrations of these elements are determined by the net effect of enriching via surface segregation and depleting through surface evaporation. The inhomogeneous phase structure of the alloys used in this study enables the observation of two migration processes driven by different forces. Below the oxide dominated surface layer, the migration of Mg is driven by chemical potential gradient and is primarily perpendicular to the surface. Closer to the surface, concentration driven horizontal diffusion of the element occurs.

The deposition of a thin TiN layer has been used to probe the interface. While the deposition conditions of TiN coatings affect the chemistry of the coatings, substrate surface conditions determine how well bonding is achieved between the film and substrate. The height difference between silicon particles in the eutectic phase and the primary aluminium phase of the casting alloys provides surface roughening and optimal adhesion through mechanical interlocking with the coating. This height difference is achieved by preferentially removing the surface exposed primary aluminium phases with ion bombardment.

The nature of surface aluminium oxides and hydroxides and their modification, has been further probed by studying how repeating fragments in TOF-SIMS spectra of these compounds originate. Gibbsite powder and a bayerite layer on a metal surface have been examined, before and after intercalation into their layered structure. This suggests that the weak interlayer bonding can be manipulated and allows cleavage of the outermost octahedral layers under bombardment by energetic particles. This phenomenon provides a new and particularly sensitive characterisation method, using the relative intensities of the repeating fragments in the TOF-SIMS spectra.

To my parents

To my wife, a friend and a colleague of more than fifteen years

ACKNOWLEDGEMENTS

First and foremost, my gratitude goes to my supervisors – Professor James Metson and Associate Professor Margaret Hyland. They are always very supportive both inside and outside of the academic environment. While their knowledge and enthusiasm in scientific research are inspiring, their understandings of and sympathy to everyday situations are equally encouraging. I truly hope to continue receiving such supports in future.

It is an absolute privilege that the study was one of the projects in Light Metals Research Centre (LMRC), the University of Auckland. The most obvious benefits include the vast pool of knowledge at the centre, the accesses to various resources and the relationships built up over the years. I would like to express special thanks to Professor Mark Taylor, David Cotton, Marcus Gustafsson, Dr Ronny Etzion, Tania Groutso, Linus Perander, Dr Wei Zhang and Jenny Roper for their extra helps.

Extensive lab works have been carried out in both Department of Chemistry and Department of Chemical and Materials Engineering. For those, I would like to thank not only LMRC staff but also Anh Tran, Dr Geoffrey Waterhouse, Dr Michael Hodgson, Dr Bryony James, Dr Colin Doyle and Catherine Hobbs. Outside the university, experiments were done with helps from Dr Kathryn Prince and Armand Atanacio at Australian Nuclear Science and Technology Organisation (ANSTO), Associate Professor Paul Pigram and Dr Robert Jones at La Trobe University, Dr Ben Ruck, Andrew Preston and Bart Ludbrook at Victoria University of Wellington, Dr Kia Wallwork at the Australian Synchrotron, and Professor Paul Munroe and Dr Charlie Kong at the University of New South Wales.

Last but not least, financial assistances are greatly appreciated: the University of Auckland Doctoral Scholarship, funding from Auckland UniServices Limited and the Foundation for Research Science and Technology (FRST) in the Transforming Light Metals Project – Objective 2, Australian Institute of Nuclear Science and Engineering (AINSE) Grant AINGRA06127P, and the allocation from the Australian Synchrotron and New Zealand Synchrotron Group Limited for Proposal 927.

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