THE UNIVERSITY OF NEWCASTLE

Exploratory Study Into Advanced Thermal Energy Storage Materials and Thermal Coatings for Survival in the Urban Environment

Doctor of Philosophy (Mechanical Engineering RHD Thesis)

This Research was Supported by an Australian Government Research Training Program (RTP) Scholarship

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Statement of Originality

I hereby certify that the work embodied in the thesis is my own work, conducted under normal supervision. The thesis contains no material which has been accepted, or is being examined, for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made. I give consent to the final version of my thesis being made available worldwide when deposited in the University's Digital Repository, subject to the provisions of the Copyright Act 1968 and any approved embargo.

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I hereby certify that this thesis is in the form of a series of papers. I have included as part of the thesis a written declaration from each co-author, endorsed in writing by the Faculty Assistant Dean (Research Training), attesting to my contribution to any jointly authored papers.

Signature: ____________________

Name: Samuel Matthew Reed

Preface and Acknowledgements

It is funny to think that at this point in my life, I find myself staring at my computer trying to formulate something witty and intelligent that reflects how I have gotten into the position that I find myself in. In the 30 years being on this planet, I never once thought I would be writing this as the final piece to my PhD thesis, but here I am. The biggest challenge and question that I have faced, and found myself asking throughout the last 4 years is, "what's the point?" As a person who finds life to be rather meaningless, I guess this question becomes almost impossible to answer. In order to deal with this bleak reality that I find myself floating in, I have learnt to draw some form of solace in the thought that this body of work may be meaningful and useful for others. I hope, and dream, that maybe one day this research will play a small role in the human populace surviving on this planet for just a little longer.

With all that in mind, I find myself rather thankful towards the people who have helped me arrive at this point in my life. I know that none of this work would be possible without the guidance and supervision from my supervisors Erich Kisi, Dylan Cuskelly and Heber Sugo. Thank you for steering me in the right direction, for your patience, and for letting me do whatever I wanted, no matter how ridiculous the thought was. To my parents, Rebecca and Paul Reed. Thank you for supporting me financially and for providing me a wonderful upbringing, I could not ask for better parents. To Sarah Collis, the most amazing and wonderful young women I have ever met. Your knowledge and support well exceeds your age and I am grateful and thankful for your ability to always make me feel better and to make me smile.

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List of Publications

Lead Author Publications

Reed, S., Sugo, H. & Kisi, E.H. (2017). New highly thermally conductive thermal storage media, Proceedings World Renewable Energy Congress (WREC XVI), Perth, Australia, 5-9 January 2017.

Reed, S., Sugo, H., Kisi, E., 2018. High temperature thermal storage materials with high energy density and conductivity. Solar Energy 163, 307-314.

Reed, S., Sugo, H., Kisi, E., Richardson, P., 2019. Extended thermal cycling of miscibility gap alloy high temperature thermal storage materials. Solar Energy 185, 333-340.

Reed, S., Kisi, E., 2020. Kinetics of Al_4C_3 Formation in High Temperature Thermal Energy Storage MGA through In-Situ Neutron Diffraction. In Preparation.

Reed, S., Kisi, E. Miscibility Gap Alloys with a Ceramic Matrix for Thermal Energy Storage. SN Applied Sciences 2, 2148 (2020).

Contributing Author Publications

Copus, M., Fraser, B., Reece, R., Hands, S., Cuskelly, D., Sugo, H., Reed, S., Bradley, J., Post, A., Kisi, E., 2019. On-sun testing of Miscibility Gap Alloy thermal storage. Solar Energy 177, 657-664.

Copus, M., Reed, S., Kisi, E., Sugo, H., Bradley, J., 2018. Scaling Up Miscibility Gap Alloy Thermal Storage Materials. Proceedings World Renewable Energy Congress (WREC XVI), Perth, Australia, 5-9 January 2017.

NB. *Only lead author publications were included in this thesis.*

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Nomenclature

Abbreviations

Al_4C_3	Aluminium Carbide
CSP	Concentrating Solar Power
CO	Carbon Monoxide
CO_2	Carbon Dioxide
DTA	Differential Thermal Analysis
HTF	Heat Transfer Fluid
LFR	Linear Fresnel Reflector
MGA	Miscibility Gap Alloy
MW	Mega Watts
SEM	Scanning Electron Microscopy
TES	Thermal Energy Storage
PCM	Phase Change Material
PDS	Parabolic Dish Stirling
PHES	Pumped Hydro Energy Storage
PTC	Parabolic Trough Collector
PV	Photovoltaics
QPA	Quantitative Phase Analysis
XRD	X-ray Diffraction

MGA Abbreviations

Al-Sn	Aluminium and Tin
AlN-Al	Aluminium Nitride and Aluminium
AlN-(Al-Si)	Aluminium Nitride and Aluminium 12.7% Silicon
Al_2O_3-Al	Alumina and Aluminium
C-Al	Carbon and Aluminium
C-(Al-Si)	Carbon and Aluminium 12.7% Silicon
C-Cu	Carbon and Copper
C-Mg	Carbon and Magnesium
C-Zn	Carbon and Zinc
Fe-Cu	Iron and Copper
Zr-Al	Zirconia and Aluminium

Abstract

Work presented in this research thesis provides a contribution to closing the knowledge gaps concerning thermal energy storage materials, particularly in the area of Miscibility Gap Alloys. The work herein has revealed that it is possible to create MGA modules for desired application temperatures. This was achieved by identifying suitable candidates in the required temperature ranges. It has shown that it is possible to make MGA thermal storage materials from C-Al, C-(Al-Si), C-Mg, C-Cu, AlN-Al, MgO-Al and Al_2O_3-Al.

The newfound thermal energy storage (TES) materials present high thermal conductivity (~140 W/mK for the C-Al and C-(Al-Si) systems) and energy densities in the region of 1 MJ/L for ΔT = 100 °C. This work has presented the effects of extended thermal cycling over the intended use range to test its effect on integrity, phase composition and microstructure for both the C-Al and C-(Al-Si) candidate materials. This research has thus proven that metastable immiscible materials may also be used as MGA. This is supported by the absence of X-ray diffraction peaks from the carbide Al_4C_3 in data from the cycled materials, along with their continued strong latent heat DTA signals after long thermal holds (120 h).

The work finally presents newer Miscibility Gap Alloys with a ceramic matrix. These ceramic MGA, which include; AlN-Al, AlN-(Al-Si), Al_2O_3-Al and MgO-Al systems were designed with a view to create an oxidation resistant macroscopically solid, phase change enhanced, thermal energy storage module. These MGA displayed no signs of degradation after 24 h of oxidation testing. The Al_2O_3-Al and MgO-Al systems formed not only a viable ceramic matrix material after firing, but also showed no signs of oxidation of Al after 72 h in air at 700 °C. These results open up a promising new series of thermal energy storage materials, some of which appear to have very good oxidation resistance under the test conditions.

It is expected that the knowledge gained from this research will provide a critical step towards implementing MGA thermal storage materials into concentrating solar power plants.