

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*

**Name:** *Samuel Matthew Reed*

**Discipline:** *Mechanical Engineering*

**Supervisors:** *Prof. Erich Kisi, Dr. Heber Sugo & Dr. Dylan Cuskelly*



THE UNIVERSITY OF  
**NEWCASTLE**  
AUSTRALIA

**Date:** 05/01/2021

### ***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.

**Signature:**

---

**Name:**

---

Samuel Matthew Reed

---

### ***Thesis by Publication***

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.

Finally, a large portion of gratitude is owed to Ashley Murie. Somehow, you have managed to support me emotionally from 7754 miles away, which I know was a hard task. I am grateful for you being a major part of my life, and I wonder if I would even still be here if it were not for you. Even though things did not go the way we wanted, know that I will always love and care for you, and will be forever indebted for your love and support.

I am personally thankful for receipt of a Research Training Program (RTP) Scholarship, provided by the University of Newcastle, and the Australian Government Department of Education and Training. Without this financial support, none of the work would have been possible.

## ***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<sub>4</sub>C<sub>3</sub> 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.

## Table of Contents

Statement of Originality .....	i
Thesis by Publication .....	i
Preface and Acknowledgements .....	ii
List of Publications .....	iii
Table of Figures .....	x
Nomenclature.....	xi
Abstract .....	xii
Chapter 1 .....	1
1    Introduction.....	1
1.1    Chapter Introduction .....	1
1.2    Problem Statement and Knowledge Gap .....	1
1.3    Objective and Research Scope.....	2
1.4    Structure of Thesis .....	3
Chapter 2 .....	5
2    Literature Review .....	5
2.1    Chapter Introduction .....	5
2.2    Renewable Energy .....	5
2.2.1    Wind Energy.....	6
2.2.2    Hydro Energy .....	8
2.2.3    Concentrating Solar Technologies.....	10
Parabolic Trough Collector.....	11
Linear Fresnel Receiver.....	13
Solar Power Tower.....	15
Parabolic Dish Stirling.....	16
2.2.4    Photovoltaics .....	18
2.3    Energy Storage Systems.....	20

2.3.1	Electrochemical Storage.....	20
2.3.2	Flywheels .....	23
2.3.3	Capacitors.....	24
2.3.4	Thermal Energy Storage.....	25
2.3.5	Comparison of Storage Technologies .....	36
2.4	Research Questions .....	37
Chapter 3 .....		38
3	Analysis and Experimental Techniques .....	38
3.1	Chapter Introduction .....	38
3.2	General Sample Manufacture and Methodology.....	38
3.3	Mechanical Alloying.....	40
3.4	X-ray Diffraction .....	41
3.4.1	Overview .....	41
3.4.2	XRD Procedure & Phase Identification .....	42
3.5	Scanning Electron Microscopy.....	43
3.6	Neutron Diffraction.....	44
3.7	Rietveld Refinements and Quantitative Phase Analysis .....	46
3.8	Thermal Testing.....	48
	Differential Thermal Analysis (DTA) .....	48
Chapter 4 .....		49
4	Preliminary Results .....	49
4.1	Uncovering Potential MGA Systems.....	49
4.2	Binder Selection for MGA Manufacture.....	52
Chapter 5 .....		55
5	World Renewable Energy Congress Publication .....	55
5.1	Chapter Introduction .....	55
5.2	Statement of Contribution .....	56

5.3	New Highly Thermally Conductive Thermal Storage Media .....	57
	Abstract.....	57
5.3.1	Introduction .....	57
5.3.2	Methodology.....	59
5.3.3	Results .....	62
5.3.4	Discussion .....	66
	References.....	67
Chapter 6	.....	69
6	Solar Energy – C-Al and C-(Al-Si) MGA .....	69
6.1	Chapter Introduction .....	69
6.2	Statement of Contribution .....	70
6.3	High Temperature Thermal Storage Materials with High Energy Density and Conductivity.....	71
	Abstract.....	71
6.3.1	Introduction .....	71
6.3.2	Methodology.....	75
6.3.3	Results .....	76
	C-Al MGA .....	76
	C-(Al-Si) MGA .....	80
6.3.4	Thermal Analysis.....	82
6.3.5	Discussion .....	82
6.3.6	Conclusions .....	86
6.3.7	Acknowledgements.....	86
	References.....	87
Chapter 7	.....	89
7	Thermal Analysis of Al and Al-Si MGA.....	89
7.1	Chapter Introduction .....	89

7.2	Statement of Contribution .....	90
7.3	Extended Thermal Cycling of Miscibility Gap Alloy High Temperature Thermal Storage Materials .....	91
	Abstract.....	91
7.3.1	Introduction .....	91
7.3.2	Experimental and Analytical Methodology .....	95
7.3.3	Results .....	97
	Sample Integrity.....	97
	Thermal Performance .....	101
7.3.4	Discussion .....	105
7.3.5	Conclusions .....	108
7.3.6	Acknowledgements.....	108
	References.....	108
Chapter 8	.....	111
8	Aluminium Carbide Formation in C-Al and C-(Al-Si) .....	111
8.1	Chapter Introduction .....	111
8.2	Statement of Contribution .....	112
8.3	Kinetics of Al <sub>4</sub> C <sub>3</sub> Formation in C-Al and C-(Al-Si) High Temperature Thermal Energy Storage Media .....	113
	Abstract.....	113
8.3.1	Introduction .....	113
8.3.2	Manufacture and Analysis Methodology .....	116
8.3.3	Results .....	118
	X-ray Diffraction Analysis of High Temperature Samples .....	118
	X-ray Diffraction Analysis of Low Temperature Samples.....	120
	In-situ Neutron Diffraction .....	120
	Quantitative Phase Analysis (QPA) .....	122
8.3.4	Discussion .....	123

8.3.5	Conclusion.....	125
8.3.6	Acknowledgments .....	126
	References.....	127
Chapter 9 .....		129
9	Oxygen Resistant Ceramic based MGA.....	129
9.1	Chapter Introduction .....	129
9.2	Statement of Contribution .....	130
9.3	MGA Thermal Energy Storage Materials with a Ceramic Matrix .....	131
	Abstract.....	131
9.3.1	Introduction .....	131
9.3.2	Experimental Methods .....	133
9.3.3	Results .....	134
9.3.4	Discussion .....	142
9.3.5	Conclusions .....	144
9.3.6	Acknowledgments .....	144
	References.....	145
Chapter 10 .....		148
10	Discussion, Future Work and Conclusion .....	148
10.1	Chapter Introduction.....	148
10.2	Discussion .....	148
10.2.1	MGA Systems for High Temperature Thermal Energy Storage .....	148
10.2.2	Thermal Reliability DTA .....	149
10.2.3	Kinetics - Aluminium Carbide .....	149
10.2.4	Ceramic MGA .....	150
10.3	Future Work .....	151
10.4	Conclusion .....	152
	References .....	153

Appendix I – Supplementary Rietveld and Neutron Data.....	160
AI.1     800°C C-Al and C-(Al-Si) MGA.....	160
AI.2     900 °C C-Al and C-(Al-Si) MGA .....	162
AI.3     1000 °C C-Al and C-(Al-Si) MGA .....	163

## **Table of Figures**

Figure 2.1 – Over View of a Pumped Hydro Energy Storage System in Okinawa, Japan [8]..	9
Figure 2.2 – The Four Main CSP Types [9].....	10
Figure 2.3 – Rotating Parabolic Trough Collector Field [11]. .....	11
Figure 2.4 – Linear Fresnel Plant with Thermal Storage Incorporated [17]. .....	13
Figure 2.5 –SPT Plant situated in Seville, Spain [19].....	15
Figure 2.6 – Variation in Parabolic Dish Stirling [21].....	16
Figure 2.7 – Conceptual Designs of PDS Systems with Thermal Storage Modules [21].....	17
Figure 2.8 – Photovoltaic Effect [23].....	18
Figure 2.9 – Installation Increase of Photovoltaic Cells in 2015 [23]. .....	19
Figure 2.10 - Comparison on Battery Storage vs Alternate Storage Systems [25]. .....	21
Figure 2.11 - Typical Flywheel Arrangement [27].....	23
Figure 2.12 –Characteristics of Capacitors with other Electrical Storage Devices [29].....	24
Figure 2.13 - Systems Investigated for Thermochemical Storage [33]. .....	25
Figure 2.14 - Typical Concrete Storage Layout with Heat Exchangers and Pipework [40]..	29
Figure 2.15 –Microstructure of a Fe-Cu and C-Cu MGA Respectively. ....	32
Figure 2.16 – a) Conceptual Layout of MGA and b) 1.5kW ‘Green’ Steam Turbine.....	35
Figure 3.1 – XRD Pattern of a C-(Al-Si) MGA.....	41
Figure 3.2 – a) C-Al and b) C-(Al-Si) MGA held at 800 °C for 10 hr. The Horizontal Axis Represents Degrees ( $2\theta$ ) and the Vertical Axis is a Time Measurement. Reflection Intensity is measured by Colour, Weakest to Strongest (Blue to Red).....	44
Figure 3.3 – Rietveld Refinement based on X-ray diffraction data of a C-Al MGA .....	46
Figure 3.4 – Components from the DTA Apparatus .....	47
Figure 4.1 – Oxidation of Fe Modules .....	49
Figure 4.2 – 140 x 140 C-(Al-Si) MGA Cracking .....	51
Figure 4.3 – Carbon MGA Samples with Swelling .....	53
Figure 4.4 – C-Al and C-(Al-Si) MGA Neutron Samples .....	53

## **Nomenclature**

### **Abbreviations**

---

<b><i>Al<sub>4</sub>C<sub>3</sub></i></b>	Aluminium Carbide
<b><i>CSP</i></b>	Concentrating Solar Power
<b><i>CO</i></b>	Carbon Monoxide
<b><i>CO<sub>2</sub></i></b>	Carbon Dioxide
<b><i>DTA</i></b>	Differential Thermal Analysis
<b><i>HTF</i></b>	Heat Transfer Fluid
<b><i>LFR</i></b>	Linear Fresnel Reflector
<b><i>MGA</i></b>	Miscibility Gap Alloy
<b><i>MW</i></b>	Mega Watts
<b><i>SEM</i></b>	Scanning Electron Microscopy
<b><i>TES</i></b>	Thermal Energy Storage
<b><i>PCM</i></b>	Phase Change Material
<b><i>PDS</i></b>	Parabolic Dish Stirling
<b><i>PHES</i></b>	Pumped Hydro Energy Storage
<b><i>PTC</i></b>	Parabolic Trough Collector
<b><i>PV</i></b>	Photovoltaics
<b><i>QPA</i></b>	Quantitative Phase Analysis
<b><i>XRD</i></b>	X-ray Diffraction

### **MGA Abbreviations**

---

<b><i>Al-Sn</i></b>	Aluminium and Tin
<b><i>AlN-Al</i></b>	Aluminium Nitride and Aluminium
<b><i>AlN-(Al-Si)</i></b>	Aluminium Nitride and Aluminium 12.7% Silicon
<b><i>Al<sub>2</sub>O<sub>3</sub>-Al</i></b>	Alumina and Aluminium
<b><i>C-Al</i></b>	Carbon and Aluminium
<b><i>C-(Al-Si)</i></b>	Carbon and Aluminium 12.7% Silicon
<b><i>C-Cu</i></b>	Carbon and Copper
<b><i>C-Mg</i></b>	Carbon and Magnesium
<b><i>C-Zn</i></b>	Carbon and Zinc
<b><i>Fe-Cu</i></b>	Iron and Copper
<b><i>Zr-Al</i></b>	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<sub>2</sub>O<sub>3</sub>-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  $\Delta T = 100$  °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<sub>4</sub>C<sub>3</sub> 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<sub>2</sub>O<sub>3</sub>-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<sub>2</sub>O<sub>3</sub>-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.