CHARACTERIZATION OF MARBLE WASTE AND GRAPHENE OXIDE REINFORCED LM6 ALUMINUM COMPOSITES FABRICATED BY STIR SQUEEZE CASTING PROCESS

BY

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A thesis submitted in fulfilment of the requirement for the degree of Doctor of Philosophy in Engineering

Kulliyyah of Engineering
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NOVEMBER 2021

ABSTRACT

Applications of aluminum matrix composites (AMC) in automobile and aerospace industries have been increasing due to their attractive properties such as lightweight, high specific modulus, stiffness and good corrosion resistance. However, the cost is the key factor in making composite materials due to the higher cost of reinforcement materials. The reuse of industrial waste, which is otherwise dumped as landfills, can reduce the composite production costs and the pollution levels posed by landfills. Therefore, this research aims to use industrial waste and graphene oxide as reinforcement phase materials to develop new and cost-effective AMC materials. In this study, LM6 aluminum alloy was used as a matrix phase, and industrial waste material of marble waste (MW) and a distinct novel material of graphene oxide (GO) with 5 wt % of each reinforcement were used for composite development. The hybrid stir and squeeze casting method was used to develop the new composites with the use of optimum casting process parameters derived from the DoE (Taguchi coupled with ANOVA) technique, integrated with Statistical Process Control (SPC) Excel software. Mechanical testing of developed AMC such as tensile, impact and hardness were performed according to ASTM- E8/EM8-13, ASTM- E23-16b and ASTM-E18 standards, respectively. The microstructural and morphological analysis were done using optical microscopy (OM), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD) techniques. Further, fractography analysis was performed on the tensile fractured surface of both composite materials using SEM equipped with JED-2300 Analysis Station Plus. Finally, a cost model for the composite fabrication process was developed and compared with fly ash and SiC-reinforced composite materials in order to draw valuable insights on the production cost of the new composites. From the evaluation of the DoE-ANOVA results, it was confirmed that stirring speed of 600 rpm, stirring time of 10 min, and melting temperature of 740 ^{o}C have had a significant influence on the response variables of LM6 composites. Mechanical test results showed that there was an increase of 16% in UTS for LM6+5%MW and 41.8% for LM6+5%GO as compared to LM6 aluminum alloy. For hardness property values, around 25.34% increase was witnessed in both composites equally compared to LM6 with the hardness value of 75.52, 94.66 and 94.68 (HRF) for LM6, LM6+5%MW and LM6+5%GO respectively. The enhanced mechanical properties were duly supported by the microstructures of both composites captured using OM, SEM, EDS and XRD. The degree of strengthening of LM6 aluminum alloy was determined by micrographs, chemical composition, particle size, and concentration of reinforcing phase materials. Subsequently, fractography analysis on tensile fractured composite samples showed no or minor cracks, thus observed that fracture was caused by matrix cracking, matrix cavitation, interface separation and rupture. The cost analysis demonstrated that the total reinforcement cost decreased by 44% due to the use of natural and industrial waste materials compared to fly ash and SiC reinforced composite materials. The current research reflected the concept of circular economy as applicable to the LM6 composites to maximize the usefulness of the waste materials. Therefore, the research concluded that MW and GO are prospective alternate candidates as reinforcements in the LM6 matrix phase to develop composites with enhanced mechanical properties suitable for automobile, aerospace and maritime industries.

خلاصة البحث

تتزايد تطبيقات مركبات مصفوفة الألومنيوم (AMC) في صناعات السيارات والطيران بسبب خصائصها الجذابة مثل الوزن الخفيف والمعامل النوعي العالي والصلابة والمقاومة الجيدة للتآكل. ومع ذلك ، فإن التكلفة هي العامل الرئيسي في صنع المواد المركبة بسبب ارتفاع تكلفة مواد التعزيز. يمكن أن تؤدي إعادة استخدام النفايات الصناعية ، التي يتم إلقاؤها كمدافن للقمامة ، إلى تقليل تكاليف الإنتاج المركبة ومستويات التلوث التي تشكلها مدافن النفايات. لذلك ، يهدف هذا البحث إلى استخدام النفايات الصناعية وأكسيد الجرافين كمواد مرحلة تقوية لتطوير مواد AMC جديدة وفعالة من حيث التكلفة. في هذه الدراسة ، تم استخدام سبائك الألومنيوم LM6 كمرحلة مصفوفة ، وتم استخدام مادة النفايات الصناعية من نفايات الرخام (MW) ومادة جديدة متميزة من أكسيد الجرافين (GO) مع 5٪ بالوزن من كل تقوية لتطوير المركب. تم استخدام طريقة الصب الهجين والضغط لتطوير المركبات الجديدة باستخدام معلمات عملية الصب المثلى المستمدة من تقنية DoE (Taguchi المقترنة بـ ANOVA) ، المدمجة مع برنامج Excel للتحكم في العمليات الإحصائية (SPC). تم إجراء الاختبارات الميكانيكية لـ AMC المطورة مثل الشد والتأثير والصلابة وفقًا لمعايير ASTM- E8/EM8-13 و ASTM- E23-16b و ASTM-E18 ، على التوالي. تم إجراء التحليل المجهري والمورفولوجي باستخدام تقنيات المجهر الضوئي (OM) والمسح المجهري الإلكتروني (SEM) والتحليل الطيفي المشتت للطاقة (EDS) وتقنيات حيود الأشعة السينية (XRD). علاوة على ذلك ، تم إجراء تحليل الكسور على السطح المكسور الشد لكلا المادتين المركبتين باستخدام SEM المجهز بمحطة تحليل JED-2300 Plus. أخيرًا ، تم تطوير نموذج تكلفة لعملية التصنيع المركب ومقارنته بنموذجين آخرين معززين مثل الرماد المتطاير والمواد المركبة SiC من أجل استخلاص رؤى قيمة حول تكلفة إنتاج المركبات الجديدة. من تقييم نتائج DoE-ANOVA ، تم التأكيد على أن سرعة التحريك البالغة 600 دورة في الدقيقة ، ووقت التحريك 10 دقائق ، ودرجة حرارة الانصهار البالغة 740 درجة مئوية كان لها تأثير كبير على متغيرات الاستجابة لمركبات LM6. أظهرت نتائج الاختبارات الميكانيكية أن هناك زيادة بنسبة 16٪ في UTS لـ LM6 + 5٪MW و 41.8٪ لـ LM6 + 5٪GO مقارنة بسبيكة الألومنيوم LM6. بالنسبة لقيم خصائص الصلابة ، لوحظ زيادة حوالي 25.34٪ في كلا المركبين بالتساوي مقارنة بـ LM6 بقيمة صلابة 75.52 و 94.66 و 94.68 (HRF)لكل من LM6 و LM6 + 5٪MW و LM6 + 5٪GO على التوالي. تم دعم الخواص الميكانيكية المحسّنة على النحو الواجب من خلال الهياكل الدقيقة لكلا المركبين اللذين تم التقاطهما باستخدام OM و SEM و EDS و XRD. لوحظ أن الصور المجهرية والتركيب الكيميائي وحجم الجسيمات وتركيز مواد مرحلة التعزيز تحدد درجة تقوية سبائك الألومنيوم LM6. بعد ذلك ، أظهر تحليل الكسور على عينات المركبة المكسورة الشد عدم وجود شروخ صغيرة أو شقوق طفيفة ، وبالتالي لوحظ أن الكسر كان ناتجًا عن تكسير المصفوفة ، وتجويف المصفوفة ، وفصل السطح البيني ، والتمزق. أظهر تحليل التكلفة أن التكلفة الإجمالية للتعزيزات انخفضت بنسبة 44٪ بسبب استخدام مواد النفايات الطبيعية والصناعية مقارنة بالرماد المتطاير والمواد المركبة المقواة بالكربيد. عكس البحث الحالي مفهوم الاقتصاد الدائري كما ينطبق على المركبات LM6 لتعظيم فائدة مواد النفايات. لذلك ، خلص البحث إلى أن MW و GO هما مرشحان بديلان محتملان كتعزيزات في مرحلة مصفوفة LM6 لتطوير مركبات ذات خواص ميكانيكية محسنة مناسبة للسيارات والطيران والصناعات البحرية.

APPROVAL PAGE

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DECLARATION

I hereby declare that this dissertation is the result of my own investigations, except where otherwise stated. I also declare that it has not been previously or concurrently submitted as a whole for any other degrees at IIUM or other institutions.

Mutlag Shafi Fuhaid Alaythee

Signature………………………… Date………………......

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My parents, they are forgiven God willing,

My sweetheart wife
And our children

For their love, understanding and their sacrifices
The comfort of eyes...... forever and ever

ACKNOWLEDGEMENTS

Foremost, all praises are due to Almighty Allah (SWT) for granting me the wisdom, guidance, knowledge, and strength to complete this thesis.

I would like to express my gratitude and appreciation to my thesis supervisor Prof. Dr Md Abdul Maleque, "main supervisor", a Professor in the Department of Manufacturing and Materials Engineering in International Islamic University Malaysia (IIUM), who has given constant guidance, friendly enthusiasm, constructive criticism, valuable suggestions and encouragement during the pursuit of this research. Furthermore, I wish to thank Assoc. Prof. Dr Mohamed Abd Rahman (co-supervisor) and Prof. Dr Murali Venkat (field supervisor) for their support and advice, which helped me achieve this project.

A similar appreciation goes to the Department of Manufacturing and Materials Engineering, KOE, IIUM and to my colleagues, Prof. Dr Ahmed Albulushi, Prof. Dr Adnan Abood, Dr. Pradeep Kumar Krishnan and Bader Al Meshaifry, the National University of Science and Technology, Oman for their support and cooperation.

I also appreciate the encouragement from the Department of Mechanical and Industrial Engineering of the National University of Science and Technology, Oman.

I pray to Allah (SWT), whom I owe the knowledge, strength, and determination to complete this research, to reward you and others that space could not allow me to mention.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS, ABBREVIATIONS AND NOTATIONS

Al	Aluminum
Al_2O_3	Aluminum oxide
AMC	Aluminum matrix composite
AMMC	Aluminum metal matrix composites
B_4C	Boron carbide
BN	Boron nitride
CMCs	Ceramic matrix composites
CNT	Carbon nanotubes
Cu	Copper
HB	Brinell hardness
Mg	Magnesium
MMCs	Metal matrix composites
Si	Silicon
Si_3N_4	Silicon nitride
SiC	Silicon carbide
SiO_2	Silicon dioxide
MW	Marble wastes
LM6	Aluminum alloy A413
GO	Graphene oxide
Zn	Zinc
SAAW	Scrap aluminum alloy wheels
SAC	Spent aluminum catalyzes
WEDM	Wire electrical discharge machining
CRT	Cathode ray tube
EAFD	Electric arc furnaces dust
WS_2	Tungsten disulfide
FW	Friction welding
FRP	Fibre-reinforced plastic
SEM	Scanning electron microscope
EDS	Energy dispersive x-ray analysis
UTS	Ultimate tensile strength
TCM	Total cost modelling
PM	Powder metallurgy
SQU	Sultan Qaboos University
ASTM	American Society for Testing and Materials

CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND

In light of varying design criteria and threshold values of crucial design parameters due to dynamic environmental and operating conditions, any engineering system demands its structures and components to be made up of adequately strong materials. A single metal/alloy fails to meet all the specifications and requirements in a harsh engineering environment. This aspect stimulates the need for developing new materials possessing specific unique properties to meet or exceed the engineering requirements and overcome technical challenges.

The development of innovative materials is almost like a panacea for all mission-critical problems and requirements. However, innovation lies in how the new materials are developed without much complications in processing, infrastructure, life expectancy (longevity) and cost-effectiveness. In the aerospace, transportation, automotive, and construction industries, there has been a growing demand for newer, stronger, and stiffer yet lightweight materials over the last few decades. Composite materials are produced largely to meet the growing technological needs of the automotive and aerospace sectors. (Chawla et al., 2013). Materials scientists constantly explore ways and means by which innovative and advanced materials with enhanced material properties can be developed to meet the ever-changing requirements.

Because of its improved mechanical and physical qualities, composite materials have proven to be a viable alternative material to many conventional metals and alloys since their inception. Composite materials are multiphase materials made up of metallic and nonmetallic materials that are immiscible within each other. The composites have more enhanced strengths and moduli compared to the properties of individual constituent materials. Thus, applications of composite materials have been gradually growing, constantly entering and conquering new markets. Modern composite materials make up a substantial proportion of the demand for engineered materials, ranging from consumer goods to specialized niche applications. Types of composites include polymer matrix-based, ceramic matrix-based and metal matrix-based composites (Rathod, Kumar & Jain, 2017; Sommers et al., 2010) Figure 1.1 shows the essential factors relative to the cost of the material.

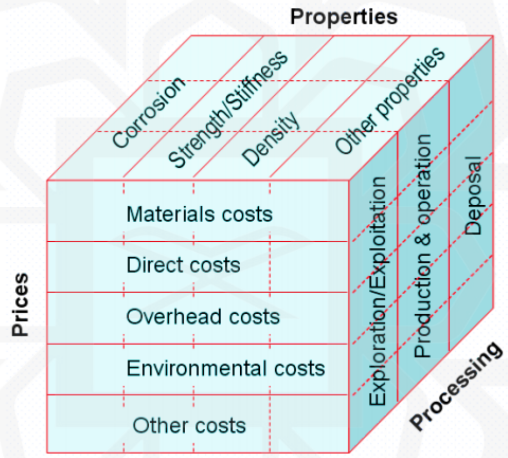

Figure 1.1 Basic Factors Relative to Cost for A Material
(Tan et al., 2008)

Due to the challenges of materials inspection, problem-solving, and constituent material reuse, processing and manufacturing composite components are more expensive with present technology. The cost, qualities, and availability related to the reinforcing phase would also contribute to the greater overall cost of creating the composite. It is estimated that the average price of aluminum alloys is 6 USD/kg, and the average price of composites is 80 USD/kg (Tan et al., 2008). For example, in a typical aircraft application (wing part), Table1.1 shows a comparison between the use of conventional aluminum alloys and AMC materials in terms of costs and component weights. Although there is a significant weight reduction (86%) and reduction in the number of pieces used (64%), it is obvious that the cost of composites has nearly doubled (93%) and is no longer comparable to that of aluminium alloys. However, increasing the mechanical qualities of composites will result in lower operating costs over time and a quicker rate of return on investment (Tan et al., 2008).

Table 1.1 Comparison of Estimated Material Parameters for Al and AMC

Materials used	**Number of parts**	**% Decrease in the number of parts**	**Weight in kg**	**% Decrease in weight**	**Estimated Cost $**	**% Increase in cost**
Aluminum	117	64%	12959.35	86%	91857.08	93%
AMC	42		1873.30		178141.63	

Therefore, it is crucial for high-intensive composite users to carefully select the materials before pressing them into manufacturing. Researchers continue to give their best to reduce the cost of composites through a range of solutions, including the reduction in the costs of constituent phase materials besides designing the processes efficiently. Several approaches could be taken to reduce composites' cost, such as single-step mixing, opting for selective reinforcements, and using cheaper reinforcements.

Because of their superior physical, mechanical, and tribological properties compared to base alloys, the applications of aluminum matrix composite materials in the automotive and aerospace industries are expanding rapidly. Because of their lower density, better wear and corrosion resistance, high strength to weight ratio, good formability, high hardness, high thermal shock resistance, high modulus, and high fatigue strength, composite materials with metal matrix materials, such as aluminum or magnesium, are finding widespread use in a variety of industries. In the automobile industry, they are used in various parts such as car bodies, pistons, valves, engine blocks, brakes, etc. Aluminum-based composites reinforced with micro/nano SiC, Al_2O_3, B_4C, TiB_2, ZrO_2, SiO_2, and graphite particles alter the microstructure, resulting in superior mechanical and physical properties suitable for automotive/aerospace applications (Koli, Agnihotri & Purohit, 2015).

Waste recycling and waste reuse are the results of the creative and innovative thinking of active researchers. These two phenomena are critical attributes of any organization that wishes to remain competitive and self-reliant in the dynamic market. For example, the Sultanate of Oman is surrounded by continuous mountains, potential natural minerals and metals such as Copper, Gold, Silver, Chromium, Lead, Nickel, Manganese and Zinc, etc. Further, the country is renowned for exporting high-quality non-metallic minerals such as marbles, granite and glass materials. Industrial wastes resulting from processing these materials are dumped in landfills. A rough estimate reports that an average of 1.6 million tons of solid waste were dumped as landfills in 2010 (Hafidh A. et al., 2019). Marble waste (MW) can be one of the potential materials for developing composite, which is also being dumped in landfills.

In summary, the costs involved in preparatory and further treatment processes for the reinforcing phase material also compound the total cost of manufacturing composites and reinforcing materials. Researchers strive hard to minimize the cost incurred in producing AMC using various strategies and techniques, including lowering the amount of reinforcement materials utilized or using low-cost reinforcing materials.

A new class of reinforcing additive called Graphene Oxide (GO), a strong and abundant mono-atomic layered substance from the graphite family, provides good mechanical properties at less wt % reinforcements. GO has unique properties such as lightweight, transparency, and superior mechanical, thermal, and hardness properties due to its honeycomb structure, making it valuable in a range of areas (Nieto et al., 2017). On the other hand, the land-fill material is a challenging issue for the government because of limited land availability and adverse environmental and public health impacts. One of the potential remedies for reducing the costs is identifying low-cost reinforcing materials without impairing the composites' desirable properties and quality. The present attempt aims to solve two issues with one solution, using industrial waste materials as a reinforcing phase in AMC, which can be used in automotive applications. The issues include the higher cost of developing AMC and environmental issues, and greenhouse gas emission due to the landfill of the industrial wastes, which are addressed in this research.

1.2 PROBLEM STATEMENT AND ITS SIGNIFICANCE

Automotive and aerospace industries demand new-age engineering materials to meet the strength, tribological and cost factors. Compared to conventional metals and alloys, composites can meet the requirements with cost challenges due to the higher development cost of composites. However, there are various composites in hand for such applications with a wide range of properties. These properties are achieved through constituent materials (both matrix and reinforcement depend on the field application), whereas the availability of the reinforcement is the key concern as it determines the significant development costs. Therefore, there is a need to identify and select new reinforcement phase materials that can reduce the composites manufacturing costs without sacrificing the materials' performance properties. Moreover, the reinforcement phase material from a waste source can reduce the cost and solve environmental problems posed by such waste materials.

A technological and environmentally sustainable approach to solid industrial waste management, disposal, reuse, and recycling has emerged as one of the world's most pressing solutions to industrial waste. Most of the wastes are dumped into landfills which take up much space and are a significant source of greenhouse gas emissions. In Oman, for example, all wastes from the marble industry are disposed of as landfills, thus polluting the environment. To date, only a few engineered land-fill sites remain among the Sultanate's more than 300 dump sites (Qureshi et al., 2018). However, MW is a promising and suitable candidate reinforcement material for the development of composites and reduce aluminum composite materials production costs because it will add no any additional costs and can contribute to solving the environmental pollution problems.

The strength of composite materials depends on several factors such as manufacturing, the existence of porosity, properties of constituent materials and wt % reinforcement. When unconventional reinforcing materials (viz. industrial or natural wastes) are used in the stir casting process, it often results in a higher porosity level in the composites, leading to inferior mechanical and physical properties(Arunachalam et al., 2019). Hence, the shift from the conventional stir casting process to a hybrid manufacturing process such as stir squeeze casting would be a promising solution for the current problem as the squeeze pressure exerted during stirring operation for the cessations of inter-atomic voids and pores of the materials, resulting in a reduction of the porosity after solidification.