Elsevier Editorial System(tm) for Materials Letters

Manuscript Draft

Manuscript Number: MLBLUE-D-18-04821R1

Title: Fibre/matrix intermetallic phase formation in novel aluminium-basalt composites

Article Type: Short Communication

Keywords: Metallic composites; Microstructure; Basalt fibres; Metallic composites; Intermetallics; Castings

Corresponding Author: Dr. Lorna Anguilano, Ph.D.

Corresponding Author's Institution: Brunel University

First Author: Onuh Adole

Order of Authors: Onuh Adole; Nilam Barekar; Lorna Anguilano, Ph.D.; Timothy Minton; Aleksander Novytskyi; Brian McKay

Abstract: A novel aluminium-basalt metal matrix composite has been produced by employing a combination of stir mixing and ultrasonication processing techniques. A study of the matrix-fibre interface has revealed the formation of Al-Si-Ca and Al-Fe-Si-Mn intermetallic compounds (IMC) with both phases displaying a polyhedral morphology. The new composite exhibited a tensile strength of 189 MPa, resulting in a 13 % improvement over the monolithic Al alloy. A 22% increase in yield strength and a 33% increase in wear resistance were also achieved, although the flexural and elastic moduli remained unchanged. It is proposed that these IMCs assist in load transfer from the matrix to the fibres.

Research Data Related to this Submission

There are no linked research data sets for this submission. The following reason is given:
Data will be made available on request

Response to Reviewers

The authors are thankful to the reviewer for pointing out some very pertinent points to improve the quality of the manuscript.

Response to individual queries is provided as follows:

1. Although fracture micro graphs have been presented and they are essential for the paper, at least a single optical micro graph of the composite may be given for the reader to see the distribution of the fibers and the nature of the matrix. Only one sentence in 3.2 mentions indirectly that the fibers agglomerated. Fiber agglomeration is well taken due to the mixing technique used but how much the agglomeration was reduced by application of ultrasonic could be of interest to some readers.

Although this study did not focus on quantifying the reduction of fibre agglomerates as a direct result of ultrasonication, optical microscopy of interval casts of the slurry before and after ultrasound treatment show deagglomeration is aided by the acoustic streaming effects. Nevertheless, low magnification micrographs are included in Fig. 1 to highlight this.

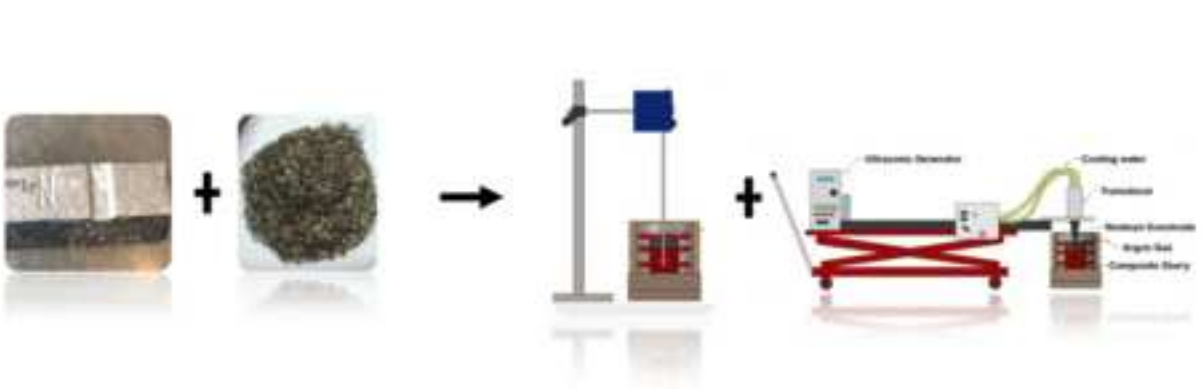
2. There is mention of 'nano indentation results of IMC in section 3.2 towards the end of the paragraph but where are the test results presented in the paper is not seen.

Apologies, this was an oversight on our part as it should have been '*micro-indentation results…*', in reference to the Vickers hardness test values around the matrix-fibre interface earlier stated.

3. Finally, the sentence in the last paragraph of the page 2 in Experimental methods " A dry sliding abrasion.....of the material' is structured badly. It needs to be re-written again.

This has now been corrected to read '*The dry abrasive wear behaviour of the composite was evaluated using a pin-on-disc wear test apparatus.'*

Graphical Abstract



Highlights

- Basalt fibres have shown reinforcement potential for metal composite development
- Al matrix-basalt fibre interaction form α-Fe intermetallics at the interface
- This chemical interaction influences the morphology transformation of intermetallics found in A356 alloys from acicular to polyhedral.
- Overall performance improvement of the composite over the reference alloy is observed.

Fibre/matrix intermetallic phase formation in novel aluminium-basalt composites

Onuh J. Adole[1], Nilam Barekar[1], Lorna Anguilano[1*], Timothy Minton[1], Aleksander Novytskyi[2], Brian McKay[1]

[1]*Brunel University London, United Kingdom*

[2]*Base Mineral Technologies (BMT) LLC, Moscow, Russia*

** Corresponding Author:*
Experimental Techniques Centre
Brunel University London Uxbridge, Middlesex UB8 3PH, United Kingdom
Phone: 44-1895-266409
Email: lorna.anguilano@brunel.ac.uk

A novel aluminium-basalt metal matrix composite has been produced by employing a combination of stir mixing and ultrasonication processing techniques. A study of the matrix-fibre interface has revealed the formation of Al-Si-Ca and Al-Fe-Si-Mn intermetallic compounds (IMC) with both phases displaying a polyhedral morphology. The new composite exhibited a tensile strength of 189 MPa, resulting in a 13 % improvement over the monolithic Al alloy. A 22% increase in yield strength and a 33% increase in wear resistance were also achieved, although the flexural and elastic moduli remained unchanged. It is proposed that these IMCs assist in load transfer from the matrix to the fibres.

Keywords: Basalt fibres, Metallic composites, Intermetallics, Cast, Microstructure

1. Introduction

Scientific interest in basalt fibres (BF) has steadily grown in recent years due to their unique properties, relatively low cost and their potential for composite development. Made from naturally-occurring volcanic basalt rock, basalt fibres were initially developed for military use; however, after their declassification in the early 1990s they attracted attention for commercial applications. This was primarily due to the fibres being inexpensive to manufacture, having high corrosion and wear resistance and possessing relatively good mechanical properties such as a Young's modulus of 78 - 110 GPa and tensile strength of 2.8 - 4.8 GPa [1].

Whilst there have been a few studies into the development of aluminium-basalt composites [2-5], they have been limited and usually stop short of investigating the matrix-reinforcement interface effects. No effort has been made to investigate the chemical and mineralogical interaction between fibre and matrix, hence limiting the knowledge of the fibre's influence on the overall performance of the

composite. The resultant fibre/matrix interface in composite materials is important with respect to the properties that are or can be attained. In this particular study, an Al-Si alloy/5 wt. % (nominal weight) basalt composite (MMC) has been developed using stir casting followed by ultrasonication. Subsequent microstructural characterisation reveals the nucleation of modified IMCs mainly on and around the fibre interface as a direct result of matrix-fibre interaction. The performance of the composites is evaluated and discussed based on preliminary results. It is assumed that these IMCs could act as a strengthening mechanism for the fibre and thus composite.

2. Experimental methods

5 wt. % of basalt whiskers (~1 cm long, ~11.50 µm ± 2.00 Ø), preheated to a temperature of 150 °C, were introduced using an aluminium foil into a graphite crucible containing 1,500 g of an A356 aluminium alloy, with a nominal composition of Al–6.8Si–0.5Mg–0.2Fe (wt. %). Distributive mixing was performed using a DC motor fitted with a 45° pitched titanium blade impeller in a heater band at 720°C for 7 minutes at a constant impeller speed of 400 rpm. An interval casting was taken at 720 ± 5 °C and poured into a pre-heated circular mould for microstructural evolution analysis.

The remaining slurry was isothermally held at 720° C for a further 10 minutes to encourage static wetting. Dispersive mixing and degassing was then performed using an ultrasonic generator employing a *Reltec* 5 kW water-cooled magnetostrictive transducer and a 20 mm diameter niobium sonotrode (5 minutes at a driving frequency of 17.5 kHz, power setting of 3.5 kW and vibration amplitude of 40 µm). After ~22 mins total processing time, the remaining composite slurry was cast (720 ± 5 °C) into a tensile test bar mould specified by ASTM B 108-806 (5 samples). The slurry temperature was monitored and maintained during processing using a K-type thermocouple.

Tensile testing was conducted in ambient temperatures (~ 24 °C) using an Instron 5559 universal electromechanical testing system. Vickers hardness tests were performed using a *Wolpert* digital Vickers tester 432-SVD with an application load and dwell time of 5 kg and 10 seconds respectively. The dynamic (i.e. adiabatic) elastic modulus was measured using the impact excitation technique (ASTM E1876-15) with an *IMCE* resonant frequency and damping analyser (RFDA). The dry abrasive wear behaviour of the composite was evaluated using a pin-on-disc wear test apparatus. The sample weight loss (ΔW) was measured after each test to a 0.001g accuracy from which the wear volume loss (mm^3) was

estimated. The wear surface structure was analysed using a *ZYGO NewView 5000* white light interferometer.

Material characterisation was carried out using a *Zeiss Supra* 35VP high resolution scanning electron microscope equipped with a field emission gun.

Table 1

Average chemical composition (wt. %) of supplied basalt fibres determined using EDS analysis

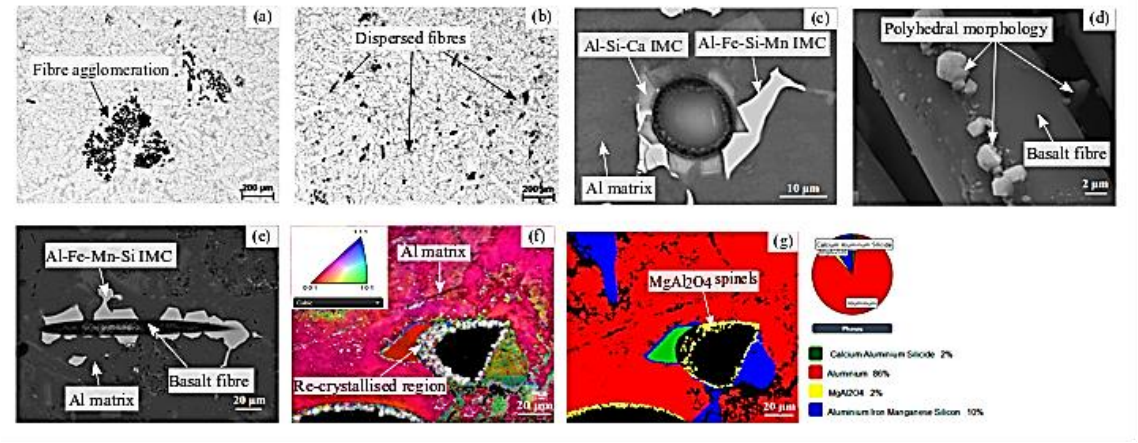
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	TiO_2
53.6	18.2	10.4	9.3	3.9	2.4	0.7

3. Results and discussion

3.1 Material characterisation

EDS analysis of the first samples cast at ~720 ºC after 7 minutes showed the presence of both an Al-Si-Ca phase with estimated formula $Al_4Si_3Ca_2$ and an Al-Fe-Si-Mn phase with estimated formula $Al_7(Fe, Mn)_2Si$. These prominent polyhedral-shaped interfacial IMCs can be seen in the BSE SEM images shown in Fig. 1 (a). The Al-Si-Ca intermetallic, however, appears to be metastable and tends to transform or dissolve after ultrasonication and a fibre-melt contact time of ~22 minutes leaving only the Fe-IMC phase remaining as seen in Fig. 1 (e).

Evaluation of both phases which appear primarily at the matrix-fibre interface indicate that they form in conjunction with the recrystallisation of the fibres which is observable as a rim around the fibres with a composition limited to aluminium, magnesium and oxygen. Recrystallisation is only initially observed at the matrix-fibre interface and gradually transforms towards the core with increased melt-fibre contact time. However, silicon was found to migrate out of the fibre into the primary aluminium, with the fibres becoming aluminium-rich. The existence of magnesium aluminate ($MgAl_2O_4$) spinels (MAS) at the rim of the fibre shown in Fig. 1(d) is possibly due to the reaction: $3Mg + 4Al_2O_3 \rightarrow 3MgAl_2O_4 + 2Al$.

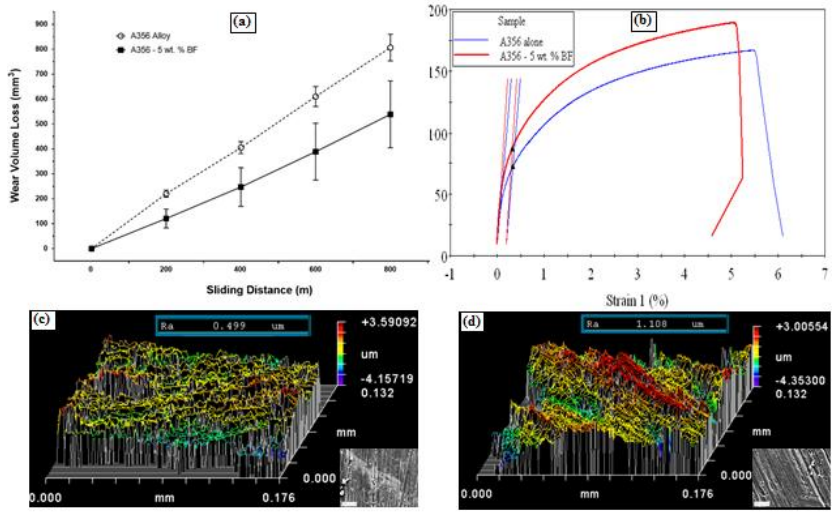


The recrystallisation of the basalt fibres is initiated by the oxidation of divalent cations as they diffuse from the fibre core to the surface creating a nanocrystalline layer which ensures an increase in the density of nucleation sites for the Fe-rich intermetallic as also reported by Gutnikov *et al.* [6]. EDS analysis suggests Mg^{2+} is the first divalent cation to migrate to the surface of fibre surface where it forms the $MgAl_2O_4$ spinels. Using planar disregistries, Cao and Campbell [7] showed that the fcc structured $MgAl_2O_4$ spinel (lattice parameter a = 0.8080 nm) could be a good substrate for the nucleation and growth of Fe IMCs due to a good lattice match. The less desirable needle-like Fe IMCs initially observed in the A356 alloy before fibre addition appear to transform to the preferred polyhedral IMC after fibre/matrix chemical interaction. This transformation could prove beneficial as phase size and morphology play key roles in the performance of a material. In addition, the resultant microstructure could also be modified due to the presence of the fibres; Li et al [9] have reported the potency of $MgAl_2O_4$ as an enhanced heterogeneous nucleation site for α-Al which could lead to significant grain refinement.

3.2 Mechanical properties

Fig. 2 (b) shows the stress-strain curve of a composite sample exhibiting a tensile strength of 189 MPa and proof stress $R_{p0.2}$ of 88 MPa compared to 167 MPa tensile strength and $R_{p0.2}$ of 72 MPa of the A356 reference sample. This translates to a 22 % improvement in the yield strength over the reference alloy, while the ultimate tensile strength increased by 13 %. Interestingly, the elastic and flexural moduli of the composite (72.15 GPa and 73.13 GPa respectively) when compared to the A356 reference alloy (72.59 GPa and 73.99 GPa) remained relatively unchanged. A further improvement in the tensile strength can be achieved by reducing fibre agglomeration which was observed on the fracture surfaces. These

fibre clusters or voids act as stress concentrators, which lead to crack initiation and propagation resulting in early failure at low loading levels. Theoretically, improvement in mechanical properties is achievable through the uniform distribution of the reinforcing basalt fibres within the matrix and the improved wettability of the fibres.



The average value of Vickers hardness of the A356–5 wt. % BF was found to be 78.9 ± 2.4 std HV5 while A356 alone recorded a value of 58.5 ± 2.4 std HV5. This 35% increase in average hardness is attributed to the diffusion of Si from the fibres into the matrix which contributes to the bulk hardness of the composite. This increase in hardness plays a defining role in the mechanical properties as elongation and ductility decreases with the increase in Si content [8]. The comparative summary of the pin-on-disc wear test results is shown in Fig. 2 (a). As expected, there is a linear increase in volume wear loss of the composite and the reference matrix alloy. However, a significant increase in the wear resistance of the composite is observed over the matrix alloy (33% improvement). This again is primarily due to the increase in hardness of the composite as this correlate well with wear resistance [10]. The formation of interfacial IMCs between matrix and fibres is also thought to contribute to the improvement of the composite's wear resistance as analysis of micro-indentation results of the IMCs and its immediate surrounding area showed high localised hardness. The values of the rough average (Ra) of the unreinforced reference alloy as seen in the oblique plots show that the roughness of unreinforced alloy (1.108 µm) is twice that of the composite (0.499 µm). The irregular surface contours of the reference alloy highlight the deep ploughing, cutting and grooving action of the SiC grit on the surface. The 3D plot of the composite, however, shows a more even surface, indicative of a better resistance to abrasive wear.

Conclusions

In summary, the chemical reaction between the basalt fibres and the A356 melt produces two distinct Al-Si-Ca and Al-Fe-Si-Mn intermetallic compounds, both adopting polyhedral morphologies. It was found that while the Al-Si-Ca IMC was metastable and dependent on processing times and temperatures, Al-Fe-Si-Mn was not and remained after full composite processing. It is postulated that the polyhedral morphology of these IMCs could act as an interlocking support mechanism for the fibres thus proving beneficial for load transfer. This preliminary study also shows great promise to enhance aluminium alloys containing high levels of Fe impurities through IMC remediation and control of the resultant microstructure. Our future work intends to focus on further improving the performance of this affordable, novel composite.

Acknowledgments

The authors gratefully acknowledge Brunel University London and the STORM Innovate UK/EPSRC project (No. 132470) for the funding towards this study. We also would like to thank Dr Roger Morrell of the Engineering Measurement and Electrical Science Division, National Physical Laboratory UK for his assistance with the dynamic elastic modulus measurements.

References

[1] J. Militky, V. Kovacic, Text. Res. J. 66 (1996) 225-229.

[2] V. Fiore, T. Scalici, G. Di Bella, A. Valenza, Compos. Part B-Eng. (2015) 74.

[3] S. Sabet, F. Akhlaghi, R. Eslami-Farsani, Lect. N. Mech. Eng. (2012)

[4] F. Akhlaghi, R. Eslami-Farsani, S. Sabet, J Compos. Mater. 47 (2012) 3379-3388.

[5] S. Vannan, S. Vizhian, R. Karthigeyan, Procedia Engineer. 97 (2014) 432-438.

[6] S. Gutnikov, M. Manylov, Y. Lipatov, B.Lazoryak, K. Pokholok, J .Non-Cryst. Solids 368 (2013) 45-50.

[7] X. Cao, J. Campbell, Metall. Mater. Trans. A, 34 (2003) 1409-1420.

[8] M. Zeren, J. Mater. Process Tech. 169 (2005) 292.

[9] H. Li, Y.Wang, Z. Fan, Acta Mater., 60 (2012) 1528-1537.

[10] H. Czichos, D. Dowson Tribol. Int. 11 (1978) 259.

Fig. 1 Optical micrographs of composite with no-ultrasonication (a) and after ultrasonication (b); BSE-SEM images and EBSD maps showing IMCs and recrystallised regions of basalt fibre (c-g).

Fig. 2 Comparative analysis of wear resistance characteristics, stress-strain curves and interferometric surface roughness images of composite and reference alloy.

Revised Figure 1

Click here to download Figure: Fig. 1 revised.eps

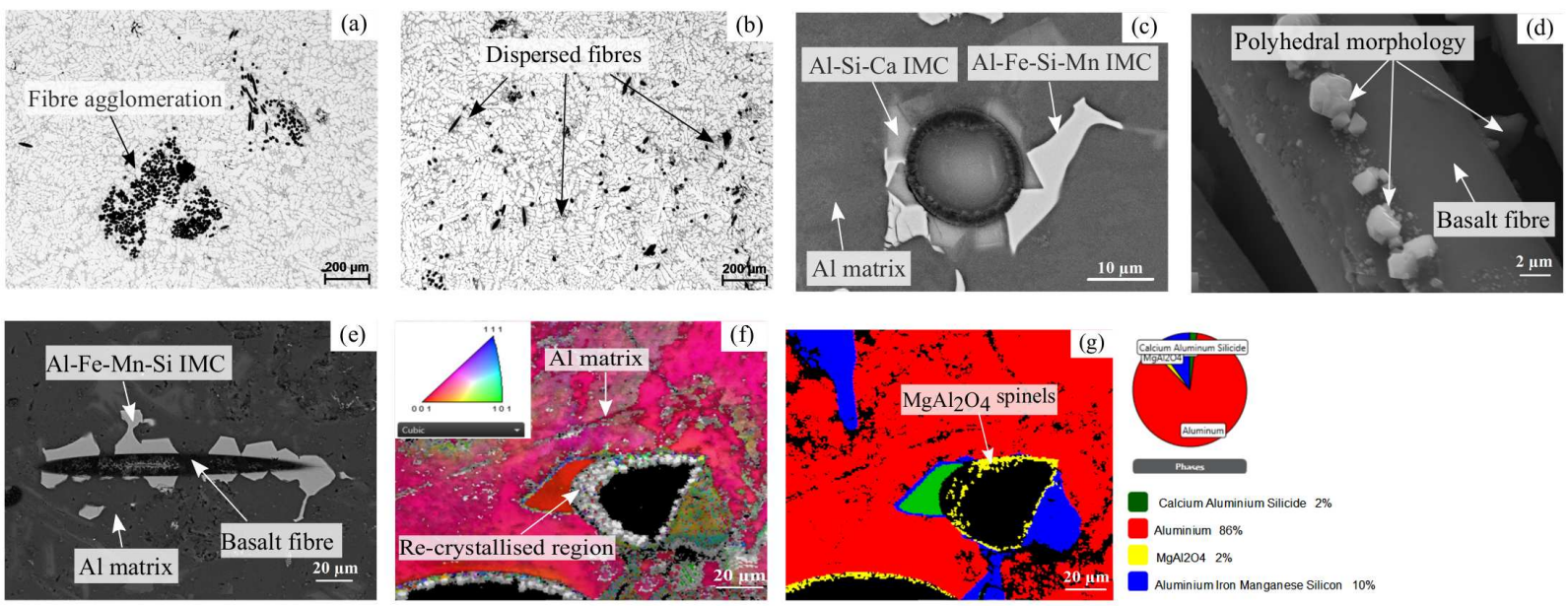
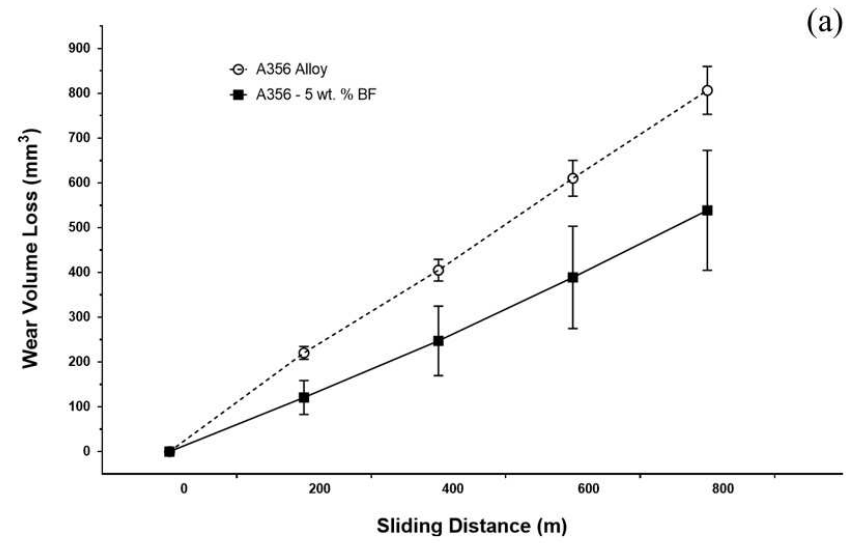
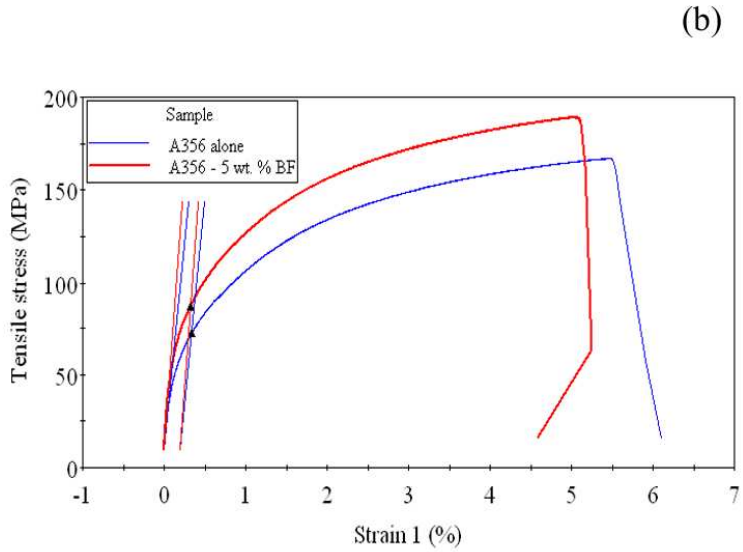
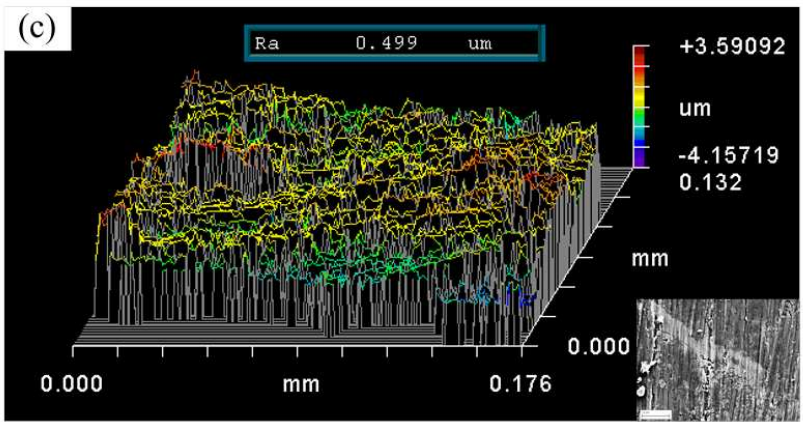


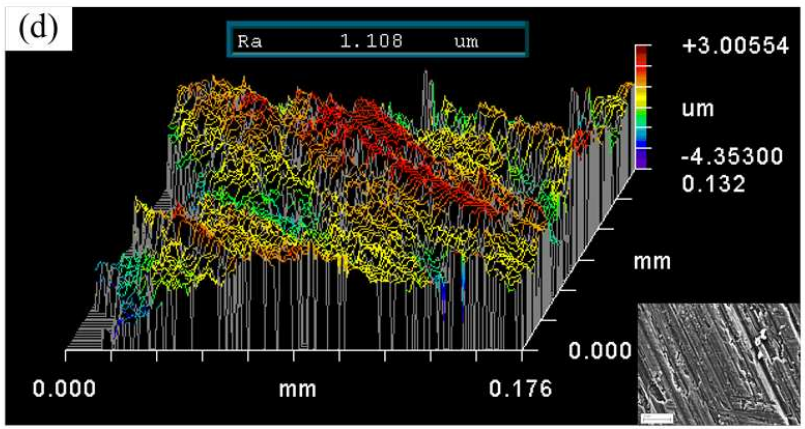
Figure 2

Click here to download Figure: Fig. 2.eps









***Declaration of Interest Statement**

Author Declaration

We wish to draw the attention of the editor to the following facts which may be considered as potential conflicts of interest:

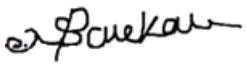
- Patent application by the authors, 'Aluminium and basalt fibres composite', GB patent application number 1714401.5
- The work was performed with funding from Innovate UK/EPSRC (Project no. 132470)

We confirm that we have given due consideration to the protection of intellectual property associated with this work and that there are no impediments to publication, including the timing of publication, with respect to intellectual property. In so doing we confirm that we have followed the regulations of our institutions concerning intellectual property.

We understand that the corresponding author is the sole contact for the editorial process (including Editorial Manager and direct communications with the office). He/she is responsible for communicating with the other authors about progress, submissions of revisions and final approval of proofs. We confirm that we have provided a current, correct email address which is accessible by the corresponding author and which has been configured to accept email from brian.mckay@brunel.ac.uk

Signed by all authors as follows:

Onuh Adole 

Nilam Barekar 

Lorna Anguilano 

Timothy Minton 

Brian McKay 

Aleksander Novitsky