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Research paper

Characterization of in Situ Zirconium Diboride (Zrb_2) Reinforced by Aluminium-Copper (Al-Cu) Metal Matrix Composites

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Abstract

Aluminium matrix composites by way of *in-situ* reaction has arisen as a preference conducive to knock out imperfections and defects exiting within *ex situ* MMC. In the present work, Al-Cu-ZrB_2 have been develop through *in situ* reaction which boost mechanical properties over dispersion strengthening together with grain refinement obtained by the existence of each particulates inside the melt all along solidification. Al-Cu reinforced among different proportion of ZrB_2 (0, 3 and 6 wt. %) synthesized using *in situ* fabrication at 800 °C of molten aluminum-copper alloys by inorganic salts K_2ZrF_6 together with KBF_4. The amalgam were specified using XRD, FESEM together with mechanical test on appropriately sectioned and metallographically prepared surface to examine and inspect phase distribution, hardness together with tensile properties. From result acquired, raised ZrB_2 amount will increase rate of tensile and hardness characteristics of Al-Cu alloy. XRD patterns exposed development of ZrB_2 particulates without existence of unspecified other compounds. Most of ZrB_2 granular were located near grain boundaries of Al dendrites. Microstructural analysis exposed the homogeneous and consistent allocation of second phase particles, clean interface and favorable bonding. It is support that ZrB_2 molecules are predominantly in nano size among hexagonal either tetragonal shape, yet minor molecules in micron size are also noticed. For that reason, composite synthesized using *in situ* techniques exhibit homogeneous distribution of reinforcing tend to be superlative associated within clean interface along the metallic matrix. In order to accomplish better mechanical features, it is necessary to regulate and control phase arrangement all along fabrication of Al-Cu with higher contents of ZrB_2.

Keywords: *Metal Matrix Composites, in situ, Aluminium-Copper (Al-Cu), Zirconium Diboride (ZrB_2), casting technique*

1. Introduction

Accelerated evolution of Metal Matrix Composite where it is coming out of reinforcement of durable ceramic assimilated toward metal matrix. It be expressed by non-metallic reinforcement constituted inside metallic matrix which is supports thousands enhancement [1]. Frequently, matrix is the predominant stage of composites by reason of its excellent in characterization which is manages to grasp and grip reinforcing phase along distributed load and force with it. The reinforcement is highly significant as well involve far-reaching due to it actually figure which is naturally build-up synchronic to the mechanical features, cost along achievement of compound itself [2] Significant focal point is on develop light weight component including upgrade mechanical behaviors for automobile together with marine utilization. As far as now, very less facts are accessible upon fabrication of aluminium based components applying Al-Zr together with Al-B alloys through the medium of *in situ* reaction. By the reason of that, this research concerned with metal matrix composites and more particularly on AMCs. *In situ* approaches have being tryout to manufacture AMCs, which is may contribute to greater adhesion interface together with favored mechanical features. *In situ* Al-based composites were expending to embellish mechanical features along dispersion strengthening together with grain refinement acquired by existence of particulates within the melt all along solidification. [3]

Aluminium matrix composites have been broadly consumed in the role of contact supports, frictional break parts, which is by reason of their superior connection of great mechanical strength together with thermal conductivity. Capital benefits of AMCs as to unreinforced element are regulate mass which is particularly consumed in reciprocating operations also enhance stiffness whilst diminish the density itself [4]. The synthesis of not heavy weight, environmental resistance as well as suited mechanical properties which is strength along with impact resistance has contrived aluminium alloys well functional for apply as matrix component.

In such conditions, AMC are frequently fabricated by liquid metallurgy by the route of *ex situ* technique, in whichever earlier created reinforcements then added into the molten alloy to enhance mechanical durability of matrix. Notwithstanding, this ordinary method encounter a number of pitfalls such as irregular dispersion, weak isometric feature together with development of interfacial reaction products [5].

Composites organized by above-mentioned methods endured from variety complexity such as thermodynamic shortcoming of reinforcement centrals of matrix, breakable reinforcement and matrix interface with inconsistent dispersion of reinforcement elements together with loss of better inflate temperature mechanical characterizations. To bear these difficult situations, writers came up within *in situ* preparation compound. *In situ* technique demonstrates a few improvements compare *ex situ* method. By carefully regulating kinetic reactions betwixt elements in molten alloy, homogenous dispersion grain, superior bonding together with enhance thermodynamic compatibility enclosed by reinforcement and matrix manage be accomplished [6, 7]

Advanced leaning have being prevailed applying particular reinforcements like titanium boride [8, 9], boron carbide [10], aluminium dioxide [11], titanium oxide [12], strontium [13] and silicon nitride [14] for production of PMMCs. Surrounded by numerous reinforcements inspected till date, ZrB_2 stay the course as a trendy and well-known component within tough bonding, extraordinarily great melting point, superior hardness together with strength along with excellent thermal conductivity and thermal shock protection, to get along as suitable applicant in demanding conditions correlated with aerospace industry [15]. TiB_2 and ZrB_2 have been extensively applied as reinforcements since their high thermodynamic stability with Al [16]. Aside from TiB_2, ZrB_2 is additional potentiality boride nominee as reinforcement of AMC alloy. The consequence of *in situ* created ZrB_2 grain on microstructure along with mechanical features of Al alloy was inspected by Liu *et al*. [17]. Inclusions of ZrB_2 have proven enhanced wear resistance together with hardness in another Al alloy component [18]. Not only that, Dinaharan mentioned that ZrB_2 particulate is an appropriate alternative of election in order to strengthen AMCs due to outstanding melting point, hardness, and electrical conductivity [19]. ZrB_2 granular is an acceptable and favorable choice in order to support AMCs owing to good wear resistance, extreme melting point, great hardness, superior thermal together with electrical conductivity [20]

The intention of this research is to establish modern and unique aluminium matrix composite that have exceedingly greater strength in mechanical operations and applications. For this scope, an attempt has been compassed to invent Al-Cu/ZrB_2 *in situ* composite using casting fabrication form K_2ZrF_6 and KBF_4 as starting components. The microstructural features and mechanical properties were examined in detail.

2. Experimental

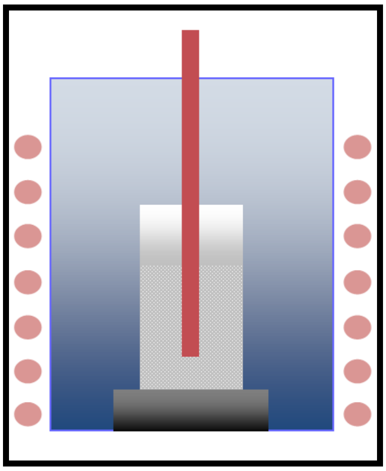

Fig. 1: Schematic diagram composite preparation in furnace

Al-Cu alloy including a couple of inorganic salts which is K_2ZrF_6 and KBF_4 were consume as raw components in order to formulate the compounds with 3 wt. % and 6 wt. % ZrB_2. Inorganic salts were dehydrated first to cut out the moisture. Concoction of K_2ZrF_6 and KBF_4 was brought in into molten alloy at 720 °C. Afterwards stirred using graphite stirrer around 800 °C for about 30 mins as well as degassing using hexachloroethane (C_2Cl_6), melted compound cast inside a preheated stainless steel mould in favors of synthesized ZrB_2 using *in situ* methods at 250 °C. Reactions during melting manage to be summarized as follows, which directly result in creation of ZrB_2 in melt.

Liquid metal frequently stirred to diminish the segregation of reinforcement particles and also to simplify the *in situ* fabrication. Afterwards, molten aluminium poured into preheat die. Casting were taken with different content of ZrB_2 particulates such as 0, 3, 6 wt. %. Specimens from the castings machined to required size to meet with microstructural analysis together with mechanical testing. Specimens grounded and polished using standard metallographic techniques; 200 grits SiC paper until 1200 grit paper and finally fine polished using diamond suspension before etched with Keller's reagent.

Polish mechanism will clear away entire left-over scratches and blemishes together with develop glossy and flat surface upcoming for electron microscopic examination. There obtained three class of size diamond slurry used which is 1μm, 3μm and 6μm. The polishing mechanism begun with 6μm diamond slurry and proceed with 3 μm and 1 μm at last. Keller's reagent dissolvent must be prepared using hydrochloric acid, HCl, nitric acid, HNO_3 together with hydrofluoric acid, HF which evaluated as well as spilled into 100ml volumetric flask. After that, distilled water will pour inside volumetric flask until calibration mark consists of mixture of Keller's reagent. Specimen then immersed into Keller's reagent two times within 5 seconds at each time and quickly flow the specimen under a stream of running tap water.

X-ray diffraction (XRD) patterns listed applying a Panalytical X-ray Diffractometers using 2θ range of 20-90°. Samples first will be etched with Keller's reagent proceeding to observe under Carl Zeiss Supra 40VP Field-Emission Scanning Electron Microscope (FESEM). A Mitutoyo MVK H1 hardness tester was selected to observe sample ability to resist metal deformation via Vickers hardness test using applied load of 10 N for 15s. Tensile samples were cut first and machined in accordance with ASTM E8M-04 standard. Tensile tests were performed on a computer controlled Instron 3382 Universal Tester machine at a constant cross head speed of 2 mm/min.

3. Results and Discussions

1.1 Formations of Al-Cu-ZrB_2 AMCs

XRD orders of fabricated composites are interpreted in Figure 2. XRD patterns validate outstanding development of metal composite. Diffraction peaks are associated to ZrB_2 grains were precisely detectable. The height of ZrB_2 peaks develop as filling is elevated. Chemical responses that developed between molten aluminum and inorganic salts; K_2ZrF_6 and KBF_4 construct ZrB_2 particulates. Generations of ZrB_2 phase influence peaks of aluminum approaching higher 2θ.

$$K_2ZrF_6 + 13Al \rightarrow 3Al_3Zr + 4AlF_3 + 6KF \quad (1)$$

$$KBF_4 + 3Al \rightarrow AlB_2 + 2AlF_3 + 2KF \quad (2)$$

$$Al_3Zr + AlB_2 \rightarrow ZrB_2 + 4Al \quad (3)$$

The regulation creation of ZrB_2 particulates is synopsized as given below: [21, 22]

- Inclusion K_2ZrF_6 together with KBF_4 to molten aluminum pointedly fabricated intermetallic compounds Al_3Zr together with AlB_2. Those admixtures are point of supply toward Zr together with B grain.
- Boron fragment will appeal to Al3Zr granular.
- Responses are proposed in the middle of Zr together with B atoms are to fabricated ZrB_2. Some breaks on surface of Al_3Zr locate stage of reaction.
- The tinier sizes of boron atoms facilitate it spread out over ZrB_2 particulates.

- The development of ZrB_2 particulates is boosted up according to dissolution of Al_3Zr particulates by fragmentation along with common cracking.
- ZrB_2 grains perfectly created afterwards reaction are accomplished.

3.2 X-Ray Diffractions Analysis

XRD patterns of Al-Cu that reinforced with 3 wt. % as well as 6 wt. % of ZrB_2 were tabulated in Figure 2. It was supported that slight ZrB_2 phases survived along with dominant Al solid solution phase in compound. Absolutely no extra impurities phase, equivalent to additional intermediate phases during melting was found. The deficiency of diffraction peaks of other phases like Cu-Zr in XRD patterns on the development of ZrB_2 imply that Zr together with B are in preference to joined to created stable ZrB_2. Diffraction peaks of Al_3Zr together with AlB_2 nonexistent in Figure 2 which proved that reaction is accomplished. Two dominant considerations that determine the reaction are holding time along with mole ratio of inorganic salts [23].

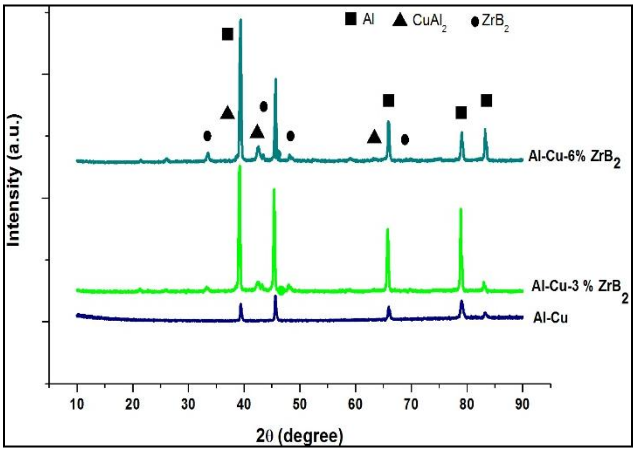

Fig. 2: X-Ray Diffraction patterns of Al-Cu reinforced with 3 wt.% and 6 wt.% ZrB_2 *in-situ* composites

3.3 Microstructure

FESEM of the sample was displayed in Figure 3. It conceivable apparently detected from Figure 3 that ZrB_2 reinforcement granular segregated near grain boundaries implying that the particular particles shifted elsewhere by growth in liquid all along solidification. It also proved that regular casting imperfections which are containing porosity together with slag are non-existence in these micrographs which are symbolic of casting characteristic [24]. The diffusion credible treated naturally being homogeneous. Diffusion of ZrB_2 particulates is direct result of solidification which followed immediately afterwards discharging the melt into the die. Assemblages of ZrB_2 granular are remarked in few locations in Figure 3. The performance of clusters developed in the course of *in situ* fabrication is dissimilar to clusters existed in *ex situ* alloys. Just after particles included outwardly, clusters created upon to some consideration inclusive of poor wettability, insufficient stirring all along density variation in the middle of aluminum alloy along with its reinforcement. Furthermore, inhabitant melt temperature falls as molecules included externally. Connections along particles in clusters are fragile which results in poor mechanical properties [25]. But particles in clusters formed by *in situ* reaction proved superior connections. Exothermal *in situ* reaction formed excellent bonding among grains inside the clusters. It is further apparent in Figure 3 that more than half of ZrB_2 particulates are noticed neighboring grain boundaries. Petty particulates positioned interior the grains. The diffusion is superlatively intergranular.

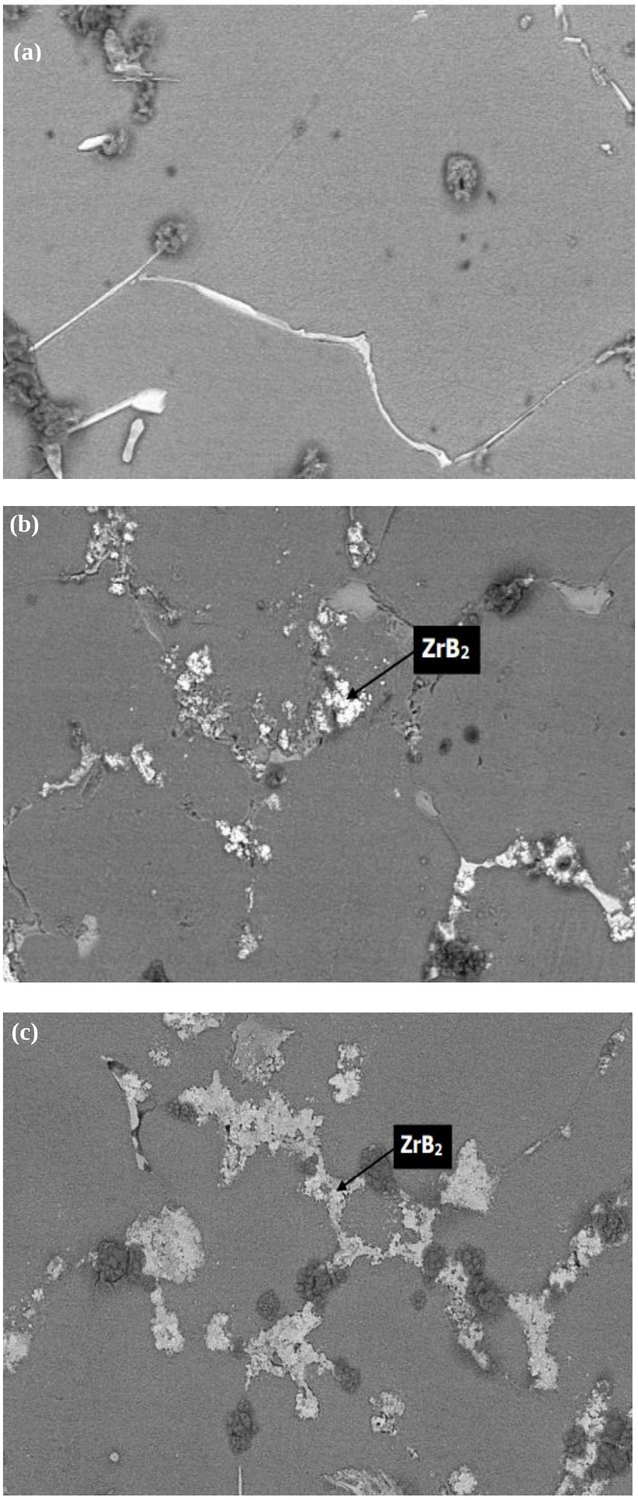

Fig. 3: FESEM images of Al-Cu *in situ* composites containing (a) 0 wt. % ZrB_2, (b) 3 wt. % ZrB_2 and (c) 6 wt. % ZrB

3.4 Tensile Behaviour of Composites

Outcomes of tensile together with hardness inspection of composite samples are displayed in Figure 4 and Figure 5 which is Al-Cu with 6 wt. % ZrB_2 demonstrated greater hardness, strain and ultimate tensile strength (UTS) related to Al-Cu reinforced with 3 wt. % ZrB_2 and unreinforced composite. The excellent interfacial connections are crated from the clear and pure interface together with good wetting ability among ZrB_2 and matrix.

The occupancy of hard ZrB_2 particles, altered of composite over *in situ* fabrication along with grain refinement could be credit for advancement in tensile strength of alloys [26]. Finest molecule diameter in alloys correlate with enhanced mechanical characteristics.

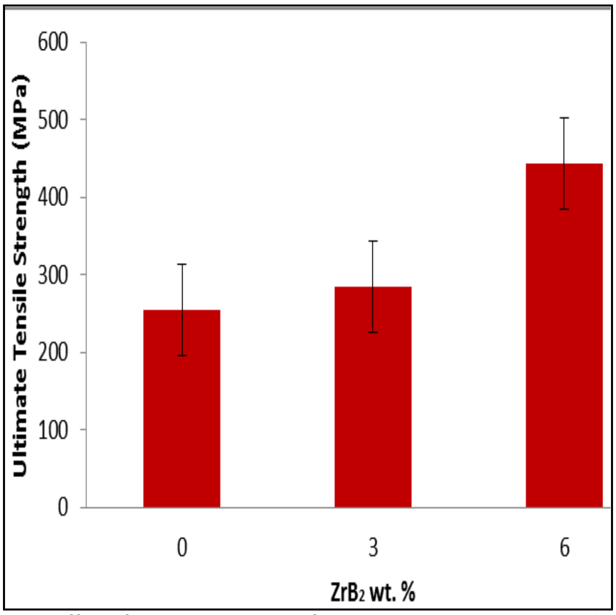

Fig. 4: Effect of weight percentage of ZrB_2 on ultimate tensile strength of A-Cu MMCs

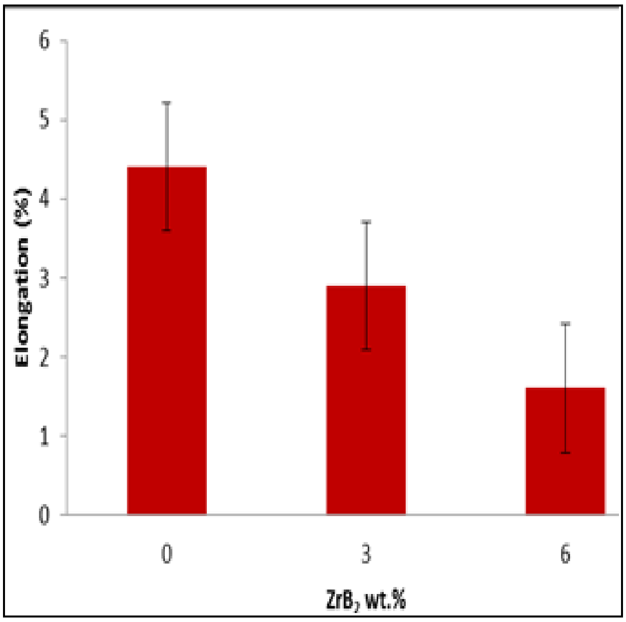

Fig. 5: Effect of weight percentage of ZrB_2 on elongation of Al-Cu MMCs

3.5 Microhardness of Al-Cu-ZrB_2

Figure 6 exhibits the evolution microhardness of *in situ* alloy with different ZrB_2 weight frictions. By its nature, microhardness boosted with increasing ZrB_2 composition. The 6 wt. % ZrB_2 alloy advertised high microhardness of 149.1 HV compare to pure Al-Cu alloy. The advancement of microhardness connected to multi-strength mechanism which is ZrB_2 diffused into Cu lattice together with enhances the load transfer from matrix to reinforcement.
All along the development solidification in cast composites, ZrB_2 constituents are going to manage to gain in dislocation density [27].
Since, *in situ* fabrication is endorsed; homogeneous connection among matrix along with reinforcement prevails in alloys. This is accessible in embellishing bulk properties of alloys. In this work, ZrB_2 perform as a load bearing features along with receives outstanding load for plastic deformation by raising hardness [28]. ZrB_2 existence a ceramic element empower component to flow in absence of undergoing deformation and defects, however when it outpaces critical value it bring about fracture with no further deformation. According to Hall-Petch equation, hardness can be upgraded by cutback in grain size [29]. Thus, grain refinement can be an impressive and efficient lead to developing hardness in ZrB_2 composite. Further, microhardness of composites boosted with increase in ZrB_2 grains.

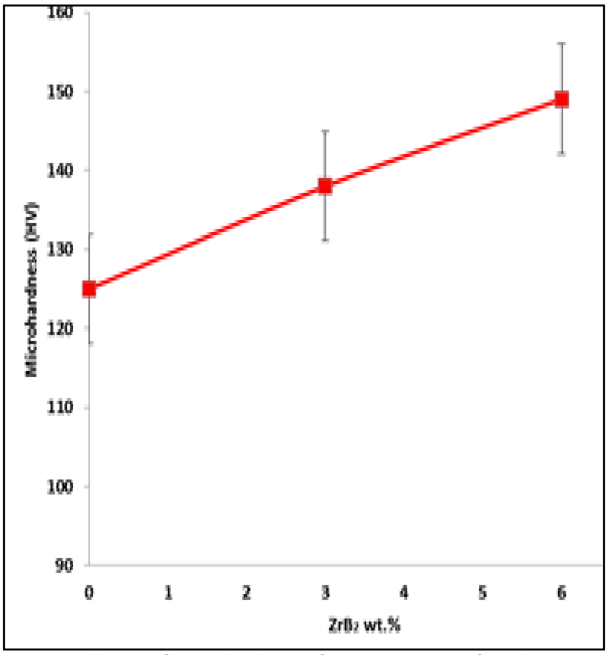

Fig. 6: Evolution of microhardness of in situ ZrB_2 reinforced composited via the weight fractions of ZrB_2 reinforcement

4. Conclusions

The successive completions imitative coming out of present work.
Al-Cu/ZrB_2 AMC consist of different percentage (0, 3, and 6 wt. %) of ZrB_2 be capable of synthesized adequately through *in situ* fabrication among molten aluminium together with inorganic salt K_2ZrF_6 and also KBF_4.
XRD patterns exposed development of ZrB_2 particulates inside composite. The nonappearance of Al_3Zr along with AlB_2 peaks proved reaction was finished perfectly.
Microstructure of composites displayed a kind of homogenous diffusion of ZrB_2 particulates.
Diameter of ZrB_2 grain particulates was in order of nano, sub-micron and also micron level which is ZrB_2 grain exhibited different morphologies which are spherical and hexagonal shapes.
The development of *in situ* ZrB_2 grain particulates enhances mechanical features which is hardness together with ultimate tensile strength. The elongation of compound reduced with a rise in ZrB_2 percentages. *In situ* ZrB_2 particulates eliminated porous and voids on the fracture surface which implies deficit in ductility of composite.

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References

[1] Babalola P. O., Bolu C. A., Inegbenebor A. O. & Odunfa K. M. (2014). Development of Aluminium Matrix Composites, *Online International Journal of Engineering and Technology Research*, vol. 2, pp. 1-11

[2] Madhusudan S., Sarcar M. M. and Mohan N. R. (2016). Mechanical Properties of Aluminium-Copper (P) Composite Metallic Materials, Journal of Applied Research and Technology, vol. 14, pp. 293-399

[3] R. Rosmamuhamadani, S. Sulaiman, M. A. Azmah Hanim, M. I. S. Ismail & M. K. Talari (2016).Mechanical and Microstructure Characterization of Aluminium-Copper (Al-Cu) Reinforced With *in situ* Titanium Diboride (TiB_2), *Key Engineering Materials*, vol. 673, pp 117-125

[4] Kai X., Tian K., Wang C., Jiao L., Chen G. & Zhao Y. (2016). Effects of Ultrasonic Vibration on The Microstructure and Tensile Properties Of The Nano ZrB_2/2024Al Composites Synthesized By Direct Melt Reaction, *Journal Alloy Compound*, vol. 668, pp. 121–127

[5] R. Rosmamuhamadani, M.K. Talari & A. Z. O Arawi (2011) Microstructure and Mechanical Properties of Al-Si cast Alloy Grain Refined with Ti-B-Sr-Sc-Mg In Humanities Science and Engineering, *IEEE Colloqium* , pp 692-695

[6] D. Bozic, J. Stasic, B. Dimcic, M. Vilotijevic, V. Rajkovic (2011) Multiple Strengthening Mechanisms in Nanoparticle-reinforced copper Matrix Composites, *Springer Link*, vol 34, pp 217-226

[7] Kumar G.N., Narayanasamy R., Natarajan, Sivaprasad K. & Sivasankaran S. (2010). Dry Sliding Wear Behaviour of AA6351-ZrB_2 In Situ Composite at Room Temperature, *Materials and Design*, vol. 31, pp. 1526–1532

[8] R.E. Ibrahim, R.Rosmamuhamadani, M.K. Talari, S. M. Yahaya, & M.I.S Ismail (2018) Corrosion Behavior of Al-Si Cast Alloy Reinforced with Titanium diboride (TiB2) and Scandium (Sc*), Journal of Engineering and Science Research*, vol. 2, pp. 1-8

[9] Ramesh C S, Keshavamurthy R, Channabasappa B H, Pramod S, (2010) Tribology International, Friction and wear behaviour of Ni-P coated Si3N4 reinforced Al6061 composites, 43, 623- 634

[10] Thomas MF Lillom,(2005),:Enhancing ductility of Al6061 + 10wt% B4C Through Equal-Channel Angular Extrusion Processing, *Materials Science and Engineering* , vol. 410, pp. 443- 446

[11] R.Rosmamuhamadani, R.E.Ibrahim, M.K.Talari, S.M.Yahaya, S.Sulaiman, M.I.S. Ismail, (2018) Characterization of Aluminium Silicon (Al-Si) Cast Alloy Refined With Titanium Diboride(TiB_2) and Scandium(Sc), *Journal of Mechanical Engineering*, vol. 5, pp.62-70

[12] Ramesh C S, Anwar Khan A R, Ravikumar N, Savanprabhu P, 2005, Wear, Prediction of wearcoefficient of Al6061-TiO2 composites, 259, 602-608

[13] S. Miresmaeili (2006) Effect of Strontium On The Oxidation Behaviors of Al-7Si,

[14] Sonber J K, Murthy T S R C, Subramanian C, Kumar S, Fotedar R K, Suri A K, 2011, International Journal of Refractoy Metals and Hard Materials, Investigation on synthesis ofZrB2 and development of new composites with HfB2 and TiSi2, 29, 21-30Journal Oxidation Metals 7(1): 107-123

[15] Surappa M. K. (2003). Aluminium Matrix Composite: Challenges and Opportunities, *Springerlink India*, vol. 28, pp. 319-334

[16] Han, Y., Liu, X., & Bian, X. (2002). In situ TiB_2 Particulate Reinforced Near Eutectic Al - Si Alloy Composites. *Composites - Part A: Applied Science And Manufacturing*, vol. 33, pp. 439–444.

[17] S. Liu, Y. Zhan, Insight into structural, mechanical and thermodynamicproperties of zirconium boride from first-principles calculations, Comput.Mater. Sci. 103 (2015) 111–115.

[18] R, Rosmamuhamadani, S. Sulaiman, S. Ismail, M. Idris, M. Arif, A. Hanim & M. K. Talari (2015) Wear Properties of Metal Matrix Composite Al-Cu ad Al-Cu-TiB_2, *Materials Sciece Forum*, vol. 819, pp. 268-273

[19] C.S. Ramesh, A. Ahamed, B.H. Channabasappa, R. Keshavamurthy (2010) Development of Al 6063–TiB_2 *in situ* composites, *Mater. Des.* vol. 31, pp. 2230–2236.

[20] M.S. Asla, M.G. Kakroudia, M. Rezvani, F.G. Fard (2015) Significance of Hot Pressingparameters On The Microstructure And Densification Behavior Of Zirconium Diboride, *Int. J. Refract. Met. Hard. Mater*. vol. 50, pp. 140–145.

[21] J. Sun, X. Zhang, Y. Zhang, N. Ma, H. Wang (2015) Effect Of Alloy Elements On The Morphology Transformation Of TiB_2 Particles In Al Matrix, Micron, vol. 70, pp. 21–25.

[22] B.S. Yigezu, P.K. Jha, M.M. Mahapatra (2013) The Key Attributes Of Synthesizing Ceramic Particulate Reinforced Al-Based Matrix Composites Through Stir Castingprocess: A Review, *Materials Manufacturing Processing*, vol. 28, pp. 969–979.

[23] Dinaharan I, Murugan N, Siva Parameswaran (2011) Materials Science And Engineering:A,Influence Of In Situ Formed Zrb2 Particles On Microstructure And Mechanical Properties , *Metal Matrix Composites*, 528, 5733-574

[24] I Diniharan and N Murugan (2012) Dry sliding wear behavior of AA6061/Zrb2 in situ composite, Transaction of Nonferrous Metals Society of China, vol. 22, pp. 873-978

[25] Sanil, B., Sumit, B., Vaibhav, G., & Suraj, R. (2017). Investigations on Microstructure and Mechanical Properties Of TiB2 Reinforced Aluminum Matrix Composites, International Journal Of Engineering Sciences And Management, vol. 7, pp. 286–289

[26] S.L. Pramod, S.R. Bakshi, B.S. Murty (2015) Aluminum-Based Cast *In Situ* Composites: Areview, *J. Mater. Eng. Perform*, vol. 24, pp. 2185–2207

[27] R. Rosmamuhamadani, S. Sulaiman, M.A. Azmah Hanim, M.I.S. Ismail & S. M. Yahaya (2016) Corrosion Characterisation of Al-Cu Reinforced *In Situ* TiB_2, *MATEC Web of Conferences*, vol. 78, pp. 1001

[28] Niels Hansen (2004), Hall-Petch Relation and Boundary Strengthening, *Scripta Materialia*, vol.8, pp.801-806