International Journal of Engineering and Advanced Technology (IJEAT)
ISSN: 2249-8958 (Online), Volume-4 Issue-6, August 2015

Synthesis and Structural Characterization of Magnesium Matrix In-Situ Composites

Md. Tusar Ali, Kazi Md. Shorowordi

ABSTRACT- ***Magnesium matrix in-situ composites were synthesized using commercially pure Mg ingot, coarse Ti and B_4C powder as starting materials. Ti and B_4C powders are mixed with zirconia balls in a plastic bottle in Ar atmosphere and the resulting mixture of these powders were compacted into a cylindrical perform. The infiltration of Mg as a matrix metal into the Ti-B_4C preform by capillary forces was done under Ar atmosphere in an electric furnace for different temperatures and holding time. Samples were prepared for phase identification and microstructural investigation. The phases formed during infiltration were analyzed using X-ray diffraction technique with Cu Kα radiation and morphology of the structure was carried out using FESEM equipped with EDX. Different types of compounds TiC, TiB_2, TiB, MgB_2, MgB_4, $B_{13}C_2$ are formed in Mg matrix during synthesis process. The dissolution of Ti and B_4C is found incomplete even at the highest synthesis temperature and holding time used in this study. The relative density is found to increase with temperature and decrease with time.***

Keywords: In-situ composites, Ti and B_4C powders, infiltration, X-ray diffraction

I. INTRODUCTION

Light weight metal matrix composites (MMCs) are of great interest due to their high specific modulus and strength as well as high wear resistance at elevated temperature. Thus, now a day, magnesium which is 35% lighter than aluminum has been considered as a potential matrix metal [1]. Magnesium MMCs reinforced with ceramic particles having high specific modulus and high wear resistance, tensile strength, low coefficient of thermal expansion and excellent electrical and thermal conductivities are potential for the automotive and aerospace applications [2-5]. Particulate reinforced composites are attractive because of ease of fabrication and isotropic properties. However the properties of MMCs depend upon the particle stability, volume fraction, size, bonding with the matrix and extent of dispersion in the matrix. Particulate reinforced Mg MMCs are generally processed by conventional methods such as powder metallurgy, spray deposition, mechanical alloying, pre-form infiltration and various casting technologies such as rheocasting, squeeze casting and compo casting. The prime challenge of these ex-situ processes is the characteristics of interfaces between matrix and reinforcement.

Manuscript published on 30 August 2015.
* Correspondence Author (s)
Md. Tusar Ali, Department of Materials and Metallurgical Engineering, Bangladesh University of Engineering and Technology, Dhaka-1000, Bangladesh,
Kazi Md. Shorowordi, Department of Materials and Metallurgical Engineering, Bangladesh University of Engineering and Technology, Dhaka-1000, Bangladesh.

In in-situ process, the reinforcement particulates are produced in the matrix metal as a result of reaction among the starting materials during infiltration. Hence, in-situ MMCs show superior mechanical properties due to the formation of ultra fine, Homogeneously dispersed and thermodynamically stable ceramic reinforcements with clean reinforcement-matrix interfaces at an effective cost [6,7]. TiC and TiB_2 ceramic particles are considered as good potential reinforcing elements in magnesium matrix due to their high melting points, good thermal and chemical stability, high hardness, low densities and excellent wear resistance [8,9]. Moreover, TiB_2 is considered as a proper reinforcement for their coherency of crystal lattice with magnesium matrix [10]. Self-propagating high temperature synthesis (SHS) and remelting and dilution (RD) are generally used in fabricating in-situ TiC-TiB_2 reinforced Mg matrix composites [11]. Synthesis of magnesium matrix composites by in-situ reactive infiltration technique can be used as an innovative process. However, a few researchers had followed this technique using Ti and C to produce TiC reinforced Mg matrix composites [12-14]. Limited work has been found in the open literature for the processing of Ti carbide and Ti borides Mg matrix in-situ composites from starting with Ti and B_4C particles by a reactive infiltration technique [12-15]. Thus, the present work has therefore been carrying out to develop in-situ Ti carbide and Ti borides reinforced Mg MMCs by infiltration technique using Ti and B_4C particles as starting materials.

II. MATERIALS AND EXPERIMENTAL METHOD

Commercially pure magnesium ingot (99.74%) was used as matrix material and Ti (average particle size 250 μm) and B_4C (average particle size 40 μm) powders were used as starting materials for synthesizing the in-situ Mg composites. Titanium and boron carbide powders with a molar ratio of 3:1 were taken with zirconia balls in a plastic bottle in Ar atmosphere in order to prevent oxidation of Ti. The powders were mixed in a ball mill with speed of 400 rpm for four hours. After mechanical blending, the resulting mixture of Ti and B_4C powders were compacted at pressure 80 MPa into green compacts of cylindrical shape of 15 mm diameter 20 mm height using hardened steel dies.

The compacted Ti-B_4C preform was placed in mild steel tube and then pieces of magnesium ingot were placed on top of the compacted preform. The steel tube was placed in a stainless steel chamber and the chamber was closed with a lid containing two openings which are used as inlet and outlet for Ar gas.

Published By:
Blue Eyes Intelligence Engineering
and Sciences Publication (BEIESP)

Stainless steel chamber was degassed before heating and then backfilled with argon gas. Synthesis process of in-situ composites by infiltration technique was carried out in an electric furnace in the presence of argon gas which is flowing at a flow rate of 5 L.min^{-1}. The synthesis process was carried out at temperatures of 800ºC and 900ºC for 1h and 4h. The heating rate was used 10ºC/min to reach synthesis temperature. At the end of infiltration, the furnace was switched off and samples were cooled down to 200ºC temperature in argon atmosphere. For phase analysis, some selective samples were analyzed by X-ray diffraction technique using Cu Kα radiation. The relative density of the composites was determined. Samples were polished by following standard metallographic technique and were investigated under field emission scanning electron microscope (FESEM) equipped with Energy dispersive x-ray (EDX).

III. RESULTS AND DISCUSSION

Ti and B_4C particle is infiltrated by magnesium at different time and temperature. To analyze the phases formed in the in-situ composite, X-ray diffraction tests were carried out on some selective samples. Fig. 1 shows the X-ray diffraction pattern of samples of Ti and B_4C powder mixture and magnesium infiltrated at 800^{0}C and 900^{0}C for 4 hour. Diffraction pattern of sample of Ti and B_4C powder mixture shows the peaks of Ti and B_4C in Fig 1a. From the X-ray diffraction pattern of the Mg composite infiltrated at 800^{0}C for 4 hour, MgB_2, MgB_4, TiC, TiB, TiB_2, $B_{13}C_2$ are identified with the addition of starting materials Mg, Ti and B_4C (Fig. 1b). Molten magnesium reacts with B_4C and formed magnesium diboride and free carbon [16]. The presence of MgB_4 peaks in the Xrd pattern are observed due to the partially decomposition of MgB_2 forming MgB_4 and Mg gas [17]. TiC is formed in-situ before the formation of titanium borides with retained titanium and enriched boron carbide ($B_{13}C_2$) due to the diffusion of free carbon towards the Ti from B_4C [18]. The formation of $B_{13}C_2$ from B_4C is also reported by Emin [19]. It is also found in X-rd pattern that TiB and TiB_2 are formed during magnesium infiltration (Fig. 1b) and TiB reacts with MgB_2 and form TiB_2. The presence of Ti and boron carbide peaks in the X-rd pattern indicates that the reaction is incomplete (Fig. 1b). The X-rd pattern of the composite infiltrated at high temperature 900^{0}C for 4 hours shows that Ti and B_4C peaks area significantly decrease with the increase of other compound peaks area (Fig. 1c). This indicates that with increasing temperature the more stable compounds are formed in-situ as the decomposition and diffusion of intermediate compounds increases.

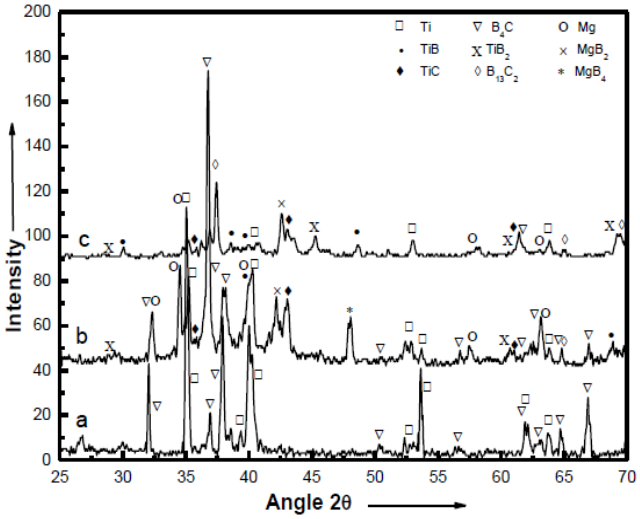


Fig. 1. X-rd patterns of (a) Ti-B_4C powder after mixing, Mg in-situ composites infiltrated at (b) 800^{0}C and (c) 900^{0}C for 4 hr

Since diffusion process of solids is time and temperature dependent, with increasing time and temperature equilibrium phases (TiB_2, TiC and Mg) in Mg-Ti-B_4C system will be formed as per thermodynamic aspects, as the free energy change of these phases are more negative than the other intermediate phases presents in the composite. But in present study, X-rd investigation revealed that at the highest temperature (900^{0}C) and time (4 hours) used, the reaction is incomplete as the Ti and B_4C peaks are evident with some intermediate phases (Fig. 1c). It is thought that the nano/sub-micron powders of Ti and B_4C instead of coarse particles can enhance the reaction and may form more stable phases within the time-temperature range used this study.

The relative density of the Mg in-situ composites are presented in Table 1. It is seen that the relative density increases with the increasing infiltration temperature and decreases with increasing time. With increasing temperature, more Mg is infiltrated into the preform by capillary action and yields high density. On the other hand, density decreases with increasing holding time due to the loss of Mg as Mg gas formed during infiltration.

Table 1 Relative density of Mg matrix in-situ composites infiltrated at different time and temperature

Time (H)	Temperature (ºC)	Relative density (gm.cc^{-1})
1	800	2.68
4	800	2.44
1	900	2.83
4	900	2.58

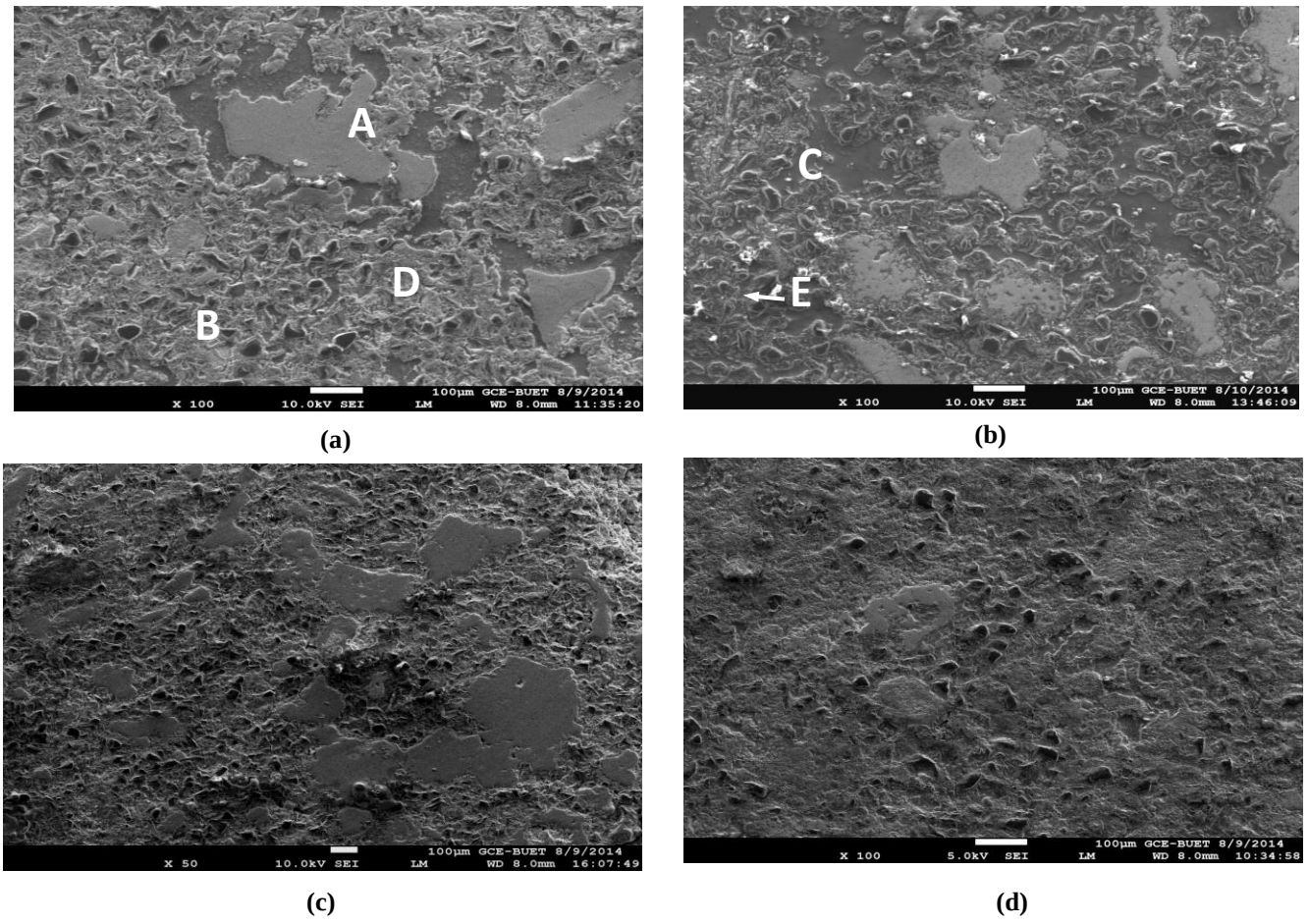
Microstructure of the magnesium based in-situ composites infiltrated at 800^{0}C for 1 and 4 hours and 900^{0}C for 1 and 4 hours is investigated using FESEM and shown in Fig. 2. Coarse Ti (250 µm) and B_4C (40 µm) are used in magnesium matrix for the processing in-situ composites. The microstructures of the four in-situ composites reveal that the distribution of reinforcements is nearly uniform in the matrix.

Published By:
Blue Eyes Intelligence Engineering
and Sciences Publication (BEIESP)

Scanning electron microscopic investigation also reveals that all the composites consist grey particles (A), black particles (B), grey at deep ditches (C), porous structure (D), white particles (E) and grey structure (F) whose size varies from a few micron to several hundred microns. EDX analysis of magnesium matrix composites was conducted on above six areas and listed in Table 2.

Table 2 Chemical composition of different phases present in Mg in-situ composites infiltrated at different temperature and time.

Phase	B (wt.%)	C (wt.%)	O (wt.%)	Mg (wt.%)	Ti (wt.%)
Grey particles (A)	-	2.31	5.86	0.22	91.61
Black particles (B)	81.36	18.44	0.15	0.02	0.03
Grey phase at deep ditches (C)	-	11.67	12.60	75.63	0.07
Porous structure (D)	14.72	17.93	14.10	3.73	49.52
White particle (E)	-	9.92	60.79	28.42	0.87



(a) (b) (c) (d)

Fig. 2. SEM micrographs of Mg in-situ composites infiltrate at (a) 800^{0}C for 1 hour, (b) 800^{0}C for 4 hour, (c) 900^{0}C for 1 hr and (d) 900^{0}C for 4 hr.

According to the EDX results, the grey dense phase (A) is identified as titanium particle while the black phase (B) is identified as B_4C particle. Grey phase (C) at deep ditches is to be infiltrated magnesium. White particle (E) in the matrix is identified as oxide of magnesium. The porous structure (D) throughout the matrix consist basically B, C, Mg and Ti, with small amount of Mg and O. This O is due to the oxidation of Mg which may be produced during polishing.

From the micrographs, it is observed that titanium particle is disintegrated with time (compare Fig. 1a and Fig. 1b) and temperature (compare Fig. 1b and Fig. 1d) and form new phases. The composites infiltrated at 900^{0}C for four hours shows a structure with small size particle. From the microstructure, it is difficult to identify the dissolution of B_4C particle as the size is much smaller than the Ti particles. However from X-rd peak intensity, it is well understood that both the Ti and B_4C particle dissolution occurs as the new phases TiC, TiB, TiB_2, MgB_2, MgB_4 are formed.

IV. CONCLUSION

Magnesium matrix in-situ composites were synthesized using reactive infiltration technique. Different types of compounds TiC, TiB_2, TiB, MgB_2, MgB_4, $B_{13}C_2$ are formed in Mg matrix during synthesis process. The dissolution of Ti and B_4C is found incomplete even at the highest synthesis temperature and holding time used in this study due to the using of coarse Ti and B_4C powders as starting materials.

Published By:
Blue Eyes Intelligence Engineering
and Sciences Publication (BEIESP)

Thermodynamically stable TiC and TiB_2 by dissolution of other less stable intermediate compounds will be formed by using submicron powder and proper synthesis parameters. The relative density is found to increase with temperature and decrease with time.

ACKNOWLEDGEMENT

The authors would like to thank Committee for Advanced Studies and Research (CASR), Bangladesh University of Engineering and Technology (BUET), Dhaka, Bangladesh for providing the financial support to carry out the present study.

REFERENCES

1. M. Kulekci. Magnesium and its alloys applications in automotive industry, The International Journal of Advanced Manufacturing Technology, Vol. 39, No. 9, 2008, pp. 851-865
2. S.F. Hassan and M. Gupta, Development of a novel magnesium-copper based composite with improved mechanical properties, Materials Research Bulletin, Vol. 37, No. 2, 2002, pp. 377-389
3. Q.C. Jiang, X.L. Li, and H.Y. Wang. Fabrication of TiC particulate reinforced magnesium matrix composites, Scripta Materialia, Vol. 48, No. 6, 2003, pp. 713-717
4. B.L. Mordike and T. Ebert. Magnesium: Properties-applications-potential, Materials Science and Engineering A, Vol. 302, No. 1, 2001, pp. 37-45
5. H.Y. Wang, Q.C. Jiang, X.L. Li, J.G. Wang, Q.F. Guan and H.Q. Liang. In-situ synthesis of TiC from nanopowders in a molten magnesium alloy, Materials Research Bulletin, Vol. 38, No. 8, 2003, pp. 1387-1392. 232
6. Y. Wang, H.Y. Wang, K. Xiu, H.Y. Wang and Q. C. Jiang. Fabrication of TiB_2 particulate reinforced magnesium matrix composites by two-step processing method, Materials Letters, Vol. 60, No. 12, 2006, pp. 1533-1537
7. L.Q. Chen, Q. Dong, M.J. Zhao, J. Bi and N. Kanetake. Synthesis of TiC/Mg composites with interpenetrating networks by in-situ reactive infiltration process, Materials Science and Engineering: A, Vol. 408, No. (1-2), 2005, pp. 125-130
8. G. Wen, S.B. Li, B.S. Zhang and Z.X. Guo. Reaction synthesis of TiB_2-TiC composites with enhanced toughness, Acta Materialia, Vol. 49, No. 8, 2001, pp. 1463-1470
9. W.J. Li, R. Tu, and T. Goto, Preparation of directionally solidified TiB_2-TiC eutectic composites by a floating zone method, Materials Letters, Vol. 60, No. 6, 2006, pp. 839- 843
10. X. Zhang, H. Wang, L. Liao, and N. Ma. New Synthesis Method and Mechanical Properties of Magnesium Matrix Composites, Journal of ASTM International, 2005, Vol. 3, No. 10. Paper No: JA1100618
11. B. Ma, H. Wang, Y. Wang, and Q. Jiang. Fabrication of (TiB2−TiC)p/AZ91 magnesium matrix hybrid composite, Journal of Materials Science, Vol. 40, No. 17, 2005, pp. 4501-4504
12. W. Cao, C. Zhang, T. Fan, and D. Zhang. In-Situ Synthesis and Compressive Deformation Behaviors of TiC Reinforced Magnesium Matrix Composites, Materials Transactions, Vol. 49, No. 11, 2008, pp. 2686-2691
13. A. Chaubey, B. Mishra, N. Mukhopadhyay, and P. Mukherjee. Effect of compact density and preheating temperature of the Al–Ti–C preform on the fabrication of in-situ Mg–TiC composites, Journal of Materials Science, Vol. 45, No. 6, 2010, pp. 1507-1513
14. D. Qun, L. Chen, Z. Mingjiu, and B. Jing. Analysis of in-situ reaction and pressureless infiltration process in fabricating TiC/Mg composites, Journal of Materials Science and Technology, Vol. 20, 2004, pp. 3-7
15. L. Chen, J. Guo, , B. Yu, , and Z. Ma. Compressive Creep Behavior of TiC/AZ91D Magnesium-matrix Composites with Interpenetrating Networks, Journal of Materials Science and Technology, Vol. 23, No. 2, 2007, pp. 207-212
16. V. Kevorkijan, and S.D. Skapin. Mg-B_4C composites with a high volume fraction of fine ceramic reinforcement, Journal of Materials and Manufacturing Processes, Vol. 24, 2009, pp. 1337-1340
17. S. Brutti, G. Balducci, G. Gigli, A. Ciccioli, P. Manfrinetti, and A. Palenzona. Thermodynamic and kinetic aspects of decomposition of MgB_2 in vacuum: Implications for optimization of synthesis conditions, Journal of Crystal Growth, Vol. 289, No.2, 2006, pp. 578-586
18. P. Shen, B. Zou, S. Jin, and Q. Jiang. Reaction mechanism in self-propagating high temperature synthesis of TiC-TiB_2/Al composites from an Al-Ti-B_4C system, Materials Science and Engineering: A, Vol. 454-455, 2007, pp. 300-309
19. D. Emin. Structure and single-phase regime of boron carbides, Journal of Review Letters B, Vol. 38, 1988, pp. 6041-6055

Published By:
Blue Eyes Intelligence Engineering and Sciences Publication (BEIESP)