PROCESSING AND MECHANICAL PROPERTIES OF IN-SITU MAGNESIUM MATRIX COMPOSITES CONTAINING NANO-SIZED POLYMER DERIVED SICNO PARTICLES

Nagaraj M. Chelliah[1], Harpreet Singh[2] and M. K. Surappa[3]

[1] Department of Mechanical Engineering, Indian Institute of Technology Ropar
Rupnagar 140001 Punjab, INDIA, cmnraj.7@gmail.com
[2] Department of Mechanical Engineering, Indian Institute of Technology Ropar
Rupnagar 140001 Punjab, INDIA, harpreetsingh@iitrpr.ac.in
[3] Department of Materials Engineering, Indian Institute of Science
Bengaluru 560012 Karnataka, INDIA, mirle@materials.iisc.ernet.in

ABSTRACT

In-situ magnesium metal matrix composites seem to be gaining attraction in next generation light weight vehicular applications since it overcomes several issues (non-uniformity of particle distribution, poor wettability and weak interfaces) associated with conventional MMCs. We introduced liquid polymer directly into the molten magnesium at 700 °C and then having it converted into 2.5 vol% SiCNO particles (mean particle size in the range of 0.5-1 μm) using a stir-casting method. Majority of the polymer derived SiCNO particles were pushed by the solidification front and as a result segregated at the grain boundaries (mean grain size in range of 50-65 μm) of in-situ composites during solidification. Therefore, the as-cast magnesium composite is subjected to single pass friction stir processing technique in order to improve the uniformity of SiCNO particle dispersion, refinement of reinforced particles (mean particle size of about 200-300 nm), and grain size (mean grain size in range of 2.5-3.5 μm) along with its mechanical properties. An enhancement of hardness, yield strength, strain to failure and strain hardening exponent in two-stage processed composites is discussed on the basis of microstructural evolution, and strengthening mechanisms.

Keywords: Magnesium, Polymer Derived Ceramics, In-situ Composites; Friction Stir Processing, Mechanical Properties

1. INTRODUCTION

Magnesium metal matrix composites have a significant potential in automotive structural application owing to the combination of high specific strength and better fuel efficiency [1]. If ceramic particles of size (d_p) are dispersed in dilute volume fraction, (V_f) then assuming cuboid shaped particles dispersed uniformly in a cube-like lattice, the yield strength of metal matrix composites is given by $G_m V_f^{1/3}$ (b / d_p), where G_m is the shear modulus, b is the Burgers vector for the dislocations. It should be noticed that finer the ceramic particles, greater the yield strength of MMCs. If the length scale of ceramic particles is in range of few nanometers (50 - 300 nm) then MMCs are termed as metal matrix nanocomposites (MMNCs). MMNCs provide far superior material performance compared to conventional MMCs with micro-sized ceramic particles. For instance, yield strength of 3.0 vol. % nano-SiC$_p$ (30 -100 nm) reinforced magnesium is comparable to that of magnesium reinforced with 30 vol% of micro-sized (20-50 μm) SiCp ceramic particles [2-3]. Moreover, strength and ductility can be substantially retained in MMNCs as volume fraction of nano-scale ceramic particles is significantly reduced. However, achieving uniform dispersion of fine scale ceramic particles in the metal matrix is often challenging task in the processing of MMCs owing to particle agglomeration by Van der Waals force of attraction [3]. Solidification processing is the most economical, viable and versatile process to fabricate MMCs for large scale manufacturing sectors [4]. Most of the technical challenges in solidification processing of MMCs can be greatly reduced by adopting in-situ composite approach by which ceramic particles are generated within the molten state via chemical reaction between the added precursor and the host metal [5]. Tjong et al [5] discussed various possibilities of producing in-situ MMCs with different matrix materials and their potential applications. Wang et al [6] fabricated the in-situ Mg-TiC composites by utilizing the exothermic reaction of the preforms consisting of Al, C and Ti powders in molten magnesium. Myriad in-situ reactions [5-6], where the ceramic particles are a product of a foreign constituent and the metal host has been discussed in the literature, choice of systems are often limited. Moreover these reaction pathways and chemical kinetics appear to be complex to understand, and hence it is not feasible for large-scale manufacturing of metal matrix composites.

Polymer derived ceramics (PDCs), so called because they are made from organic precursors which, when heated, typically, from 400 ^{o}C to 1000 ^{o}C, decompose to yield ceramics [7]. Many ceramics, both oxides and non-oxides are currently produced from polymer precursors. Investigators at the Indian Institute of Science and the University of Colorado have been collaborating to explore the possibility of fabricating polymer-derived metal matrix composites (P-MMCs) by utilizing the in-situ pyrolysis approach [8-9]. A unique feature of the P-MMC process is that all constituents of the ceramic phase are built into the polymer molecules. Therefore, no chemical reaction is required between the polymer precursor and the host metal to produce ceramic particles. Furthermore, the ins-situ pyrolysis is a highly reactive process, accompanied by the evolution of hydrogen, which fragments and disperses the micron-sized ceramic phase into nanoscale or sub-micron constituents [3]. The two critical main issues were indentified in earlier work [9] as follows: (i) the chemical reaction between polymer precursor and magnesium melt results in the formation of brittle Mg_2Si particles at pyrolysis temperature ranging from 800 to 1000 ^{o}C. These brittle Mg_2Si particles impair the ductility of resulting composite. Further, this leads to the reduction in the amount of polymer precursor available for generation of sub-micron sized SiCNO particles and (ii) most of the PDC particles are pushed away by the solidification front and as a result segregate at the grain boundaries. Such grain boundary segregation limits the enhancement in the mechanical properties of the final in-situ MMCs. Recently, we have explored two-step processing to address the existing disadvantages associated with primary processing of Mg-based in-situ MMCs derived from polymer precursor approach [10]. The intensity of formation of Mg_2Si phase, and grain boundary segregation of reinforced PDC particles were minimized by processing of in-situ composites at 700 ^{o}C and followed by FSP processing. The present paper reports on the processing and mechanical properties of in-situ magnesium matrix composites having uniform dispersion of nano-sized SiCNO particles by combining liquid state stir-casting and solid state friction stir processing techniques.

2. PROCESSING METHODS

Commercially grade Mg (99.9%) billets (supplied from Hindustan Aerospace limited, Bengaluru) was chosen as the matrix material. Poly(urea-methyl-vinyl)silazane (PUVMS) procured from Kion Corporation (USA), was utilized as polymer precursor for the reinforcement. As-received liquid polymer was introduced directly into the molten Mg in all the casting experiments. The schematic diagram of melting furnace used for fabrication of in-situ magnesium MMCs is shown in Fig. 1. 700 gm of Mg blocks were melted in a steel crucible using an electrical resistance furnace at a temperature of 700 ^{o}C. The steel crucible was continuously purged with Ar-5%SF_6 gas mixture to eliminate the flammability and risk of fire hazards with molten Mg. The melt was mechanically stirred by a 3-axial stirrer blade at 600 rpm to create good vortex in the melt. Subsequently, 3.5 wt% liquid polymer was injected into the melt and the stirring was continued for next 15 minutes in order to ensure completion of pyrolysis. After processing, the mixed molten slurry was bottom-poured into a pre-heated (at a temperature of 300 ^{o}C) rectangular split-molds made of steel. The as-cast plates (300 mm length x 100 mm width x 6.5 mm thickness) were machined out of the casting ingots for friction stir processing. A single-pass FSP was performed on as-cast composites by computer controlled (CNC) three axial vertical-type milling machine as shown in Fig. 2. The as-cast plates were initially placed, and fixed by fixtures. The cylindrical FSP tool made of H-13 tool steel had a shoulder diameter of 20 mm, and pin diameter and height of 6.5 mm and 6 mm respectively. FSP was done at constant tool rotation of 1000 rpm with transverse linear speed of 20 mm min^{-1} under ambient condition. Plunge depth of 6.1 mm was maintained.

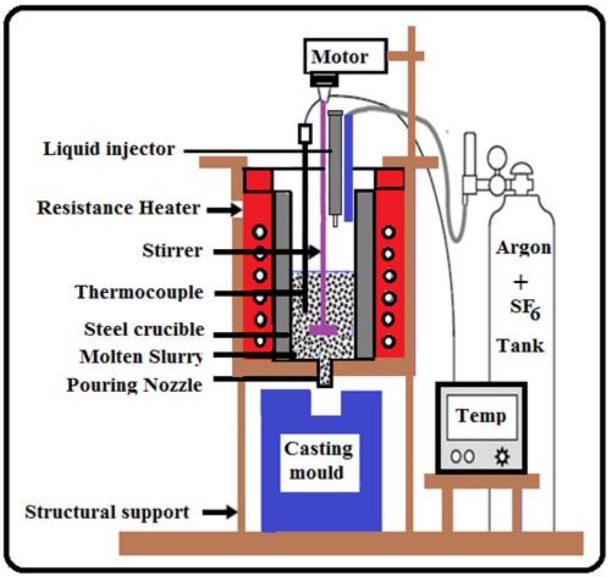

Fig 1: Schematic diagram of Mg furnace used for fabricating in-situ magnesium MMCs [10].

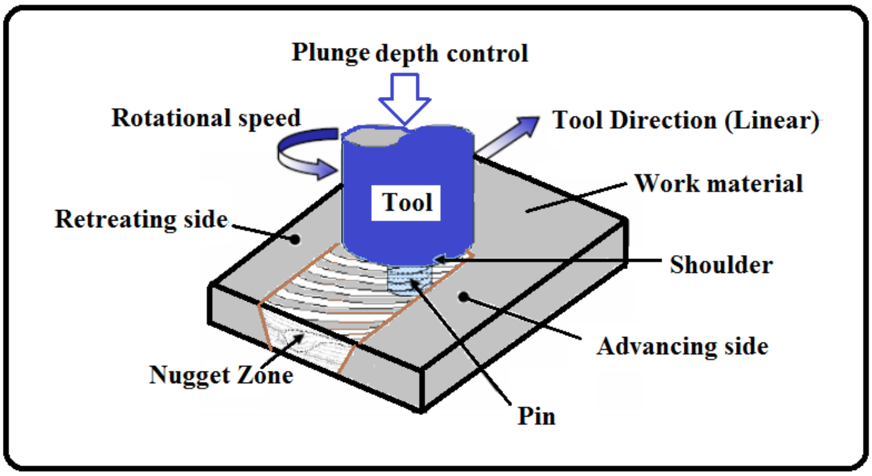

Fig 2: Schematic diagram of friction stir processing set up used for microstructural modification of as-cast magnesium MMCs.

3. MATERIAL CHARACTERIZATION TECHNIQUES

Matrix grain sizes and distribution of PDC particles in both as-cast and FS processed composites were characterized by optical microscope (Leica DM2700, Germany), scanning electron microscope (JEOL JSM-6610LV, Japan) and transmission electron microscope (Tecnai T20, FEI Company). Micro-hardness of FS processed, and as-cast composites were measured obtained using Vicker's micro-hardness tester (Wilson Instrument, United Kingdom) at a load of 500 gf (4.9 N) for a dwell time of 15 s. Each hardness value represents an average of six measurements done at different locations on the matrix. Uni-axial compression tests were performed using Tinus Olsen mechanical testing machine to record the room temperature mechanical properties at a constant strain rate of 10^{-3} s^{-1}. Compression specimen had a diameter of 4 mm, and 6.5 mm height. Values of reported mechanical properties are average of three compression tests.

4. RESULTS AND DISCUSSION

4.1 Microstructures

The average grain size of as-cast composite is found to be in the range of 50-65 μm whereas it was reduced to 2.5-3.5 μm in the case of FS processed composite (Figs 3(a) and 3(b)). The grain size refinement could be attributed to DRX process in the nugget zone during FSP. DRX process occurs by the progressive arrangement of dislocations around low-angle or high angle boundaries tending to form new grains. Further, the presence of PDC particles in the Mg matrix also accelerates the DRX kinetics due to two reasons: Firstly, particles generate higher density of dislocations within the matrix due to mismatch in coefficient of thermal expansion prior to FSP treatment. Thus pre-existence of dislocations eventually provides stored energy to initiate DRX process. Secondly, the nano-sized PDC particles suppress any abnormal grain growth due to Zener pining effect during FSP [11]. It can be seen that the as-cast composite is characterized by grain boundary segregation of PDC particles (Fig. 3(a)), whereas the FS processed composite shows uniform distribution of PDC particles throughout the magnesium matrix (Fig. 3(b)).

While the PDC particles in as-cast PL700 specimen as shown in Fig 4(a) had a platelet morphology having a width of 0.5-1 μm and length of 3-5 μm. In contrast PDC particles in FS processed PL700 as seen in Fig 4(b), seem to be near equiaxial shaped, and/or spherical morphologies with an average particle size in the range of 200-300 nm. It is evident that the refined PDC particles are redistributed uniformly throughout the nugget zone, and this is associated with severe plastic deformation during FSP. In addition, the uniform dispersion of PDC particles in the magnesium matrix of the FS processed FPL700 composites is further evident by TEM micrographs as shown in Fig 5. The severe plastic deformation within the nugget zone is expected to create fragmentation in the larger SiCNO particles leading to nano-sized particles, and stirring action arising during FSP tool aids in achieving the uniform dispersion of particles throughout the Mg matrix.

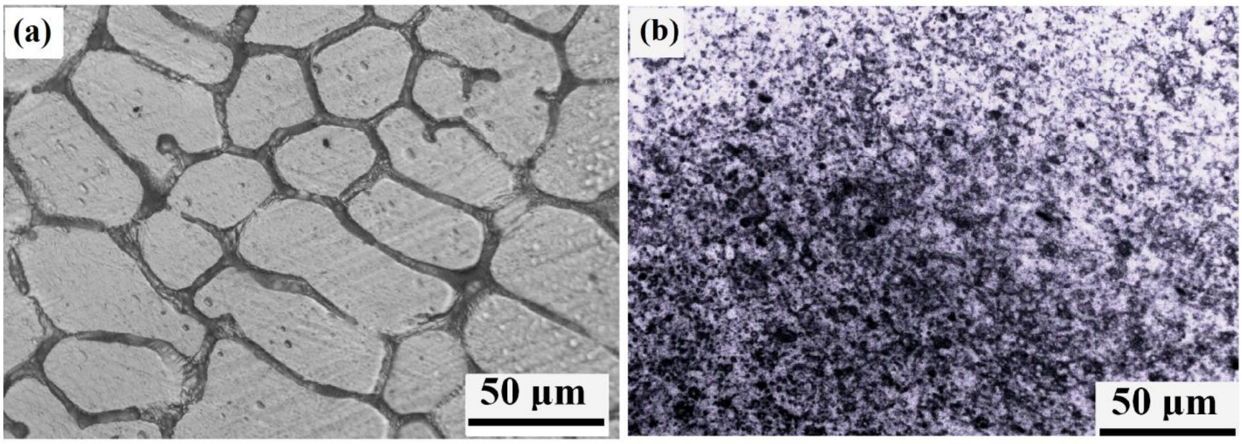

Fig 3: Microstructures of Mg matrix reinforced with polymer derived ceramic particles (a) as-cast composites and (b) FS processed composites [10].

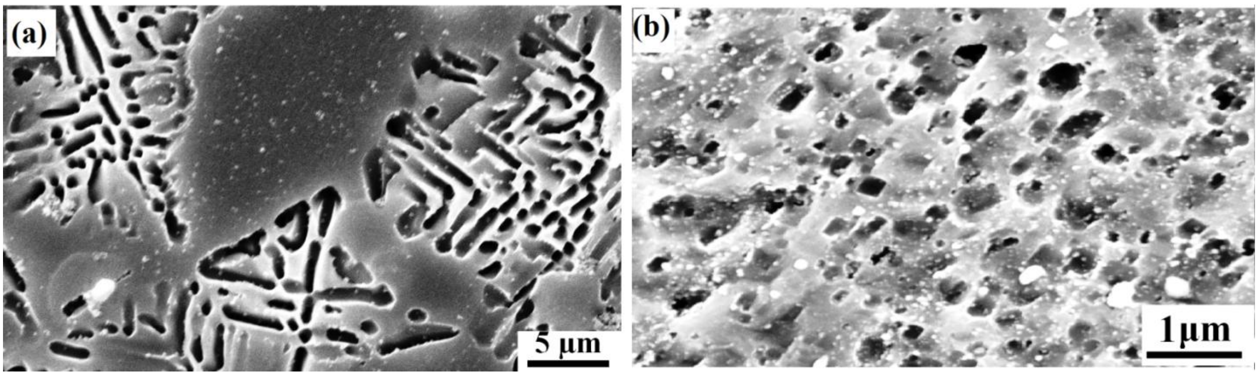

Fig 4: SEM micrographs showing distribution of polymer derived particles a) As-cast magnesium composites and (b) Nugget zone in FS processed magnesium composites [10]

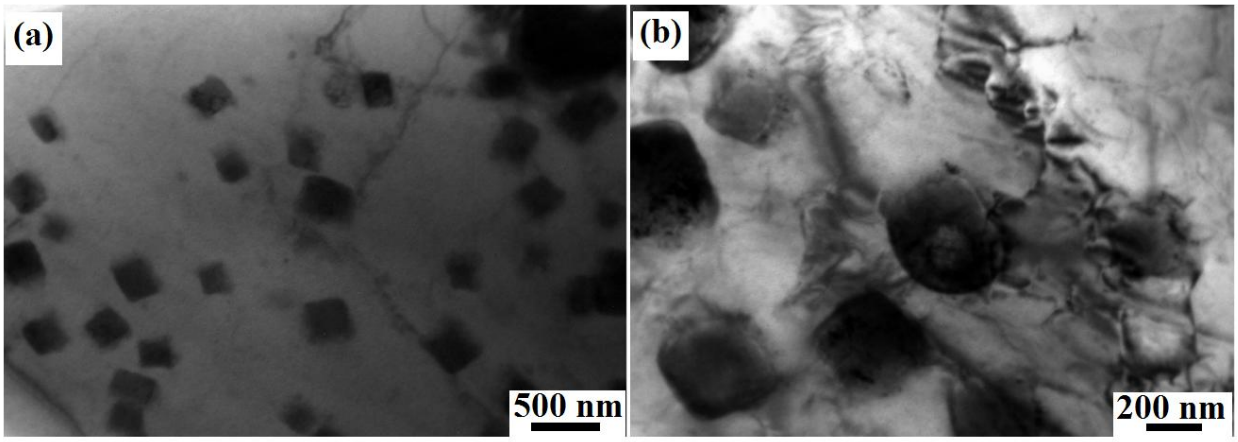

Fig 5: (a) and (b): TEM micrographs showing uniform distribution of polymer derived particles in the matrix of friction stir processed magnesium composites [10]

4.2 Mechanical properties

Hardness of FS processed composite is significantly higher compared to that of as-cast composites as seen in Table 1. For instance, the hardness value of friction processed composite specimen is enhanced by 95% as compared to that of the as-cast PL700 specimen. Compressive true stress-true strain plots show that yield strength and ultimate compressive strength (UCS) of FS processed composite is significantly higher than that of the as-cast counterpart as seen in Fig. 6. For instance, the yield strength and UCS of FL700 specimen is enhanced by 158% and 125%, respectively. The FS processed composite specimen shows increment in the value of strain to failure by 22%, and this indicates that ductility of FS processed composite specimen is retained even though its yield strength is higher. Strain hardening exponent determines how well the composites work harden with the imposed applied stress. The strain hardening exponent of FS processed composite specimen increases by 50% as compared to that of as-cast specimen. Such increases in mechanical properties could be attributed to significant refinement of both the grain size of the matrix material, and size of the PDC particles caused by FSP. Further, FSP minimizes the grain boundary segregation of PDC particles due to their uniform dispersion throughout the Mg matrix.

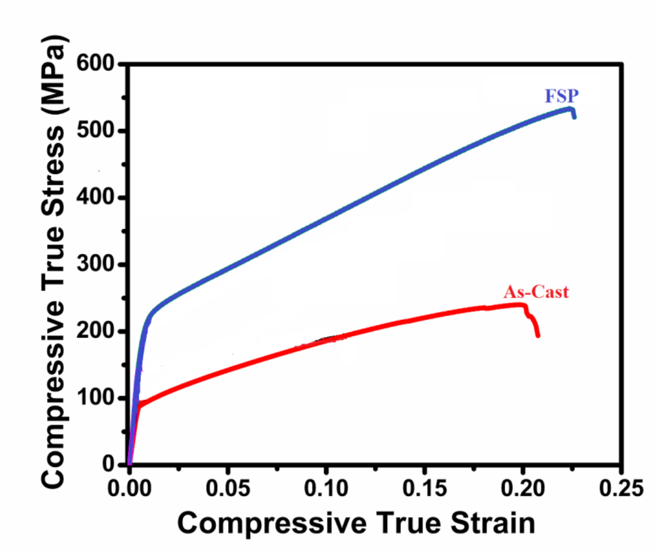

Fig 6: Compressive stress-strain curves of Mg based in-situ composites

Mechanical Properties		As-cast P-MMCs	FS processed P-MMCs
Micro-hardness	[HV0.5]	44 ± 2	86 ± 1
Compressive Yield Stress	[MPa]	85 ± 3	220 ± 5
Ultimate Compressive Stress	[MPa]	235 ± 7	530 ± 21
Strain to failure	[%]	18 ± 0.5	22 ± 0.5
Strain hardening index	−	0.30 ± 0.03	0.45 ± 0.02

Table 1: Summary of mechanical properties in P-MMCs

Basically, yield strength of the particulate MMCs can be enhanced by four different strengthening modes [12] namely: (i) Hall-Petch effect (ii) Orowan mechanism (iii) Taylor contribution and (iv) load transfer strengthening. After assessing different strengthening mechanisms, Hall-Petch mechanism was found to be the major strength enhancement contributor in both the as-cast and FS processed composites. The activation of Hall-Petch effect in the processed composites (both as-cast and FS processed condition) can be explained as follows. For the case of as-cast composites, the presence of PDC particles in the molten Mg served as heterogeneous nucleation sites and help in the nucleation of Mg grains. In addition, the grain boundary segregation of PDC particles restricts the grain growth during solidification. Both these factors contribute to considerable refinement in the grain size leading to operation of Hall-Petch effect. For instance, the average grain size of the as-cast composites is typically in the range of 50-65 μm, while it was 410 ± 25 μm for the case of unreinforced pure magnesium. After single-pass FS processing of these as-cast composites, the mean grain size is reduced further from 50 μm to 2.5 μm. As mentioned earlier, DRX process appears to be the major contributing factor in the grain refinement. Finer the grain size, higher the chance of impeding the dislocation motion at the grain boundaries which eventually leads to increase in the contribution of Hall-Petch strengthening.

5. CONCLUSIONS

In-situ magnesium matrix composites containing nano-sized SiCNO particles are fabricated by combining both the liquid- and solid-state processing routes. Liquid-state process helps to produce in-situ ceramic particles via pyrolysis of liquid polymer, while solid-state FSP aids in improving the uniformity of particle distribution, minimizing segregation, particle refinement, and refinement of grain sizes of composites. Micro-hardness, yield stress, ultimate compressive stress, strain to failure and strain hardening exponent of the as-cast composites are improved by 95%, 158%, 125%, 22% and 50% respectively after FSP. These improvements have occurred due to intense material flow and dynamic recrystallization (DRX) which are the main attributes of FSP. Hall-Petch strengthening was found to be the most dominant mechanism on enhancing the yield strength of Mg-based in-situ MMCs processed by two-stage process.

ACKNOWLEDGEMENTS

The authors would like to express their gratitude to Prof. Rishi Raj, University of Colorado, Boulder, for his valuable inputs, and for providing the precursor materials under Grant No.DMR1105347 supported by the National Science Foundation.

REFERENCES

[1] B.L. Mordike, T.Ebert, Magnesium properties-applications-potentials, Material Science and Engineering: A. **302** (2001) 337-345.
[2] H. Ferkel, and B.L. Mordike, Magnesium strengthened by SiC nanoparticles. Material Science and Engineering: A., **298** (2001) pp. 193-199.
[3] R.A. Saravanan, and M.K. Surappa, Fabrication and characterization of pure magnesium-30 vol.% SiCp particle composite. Material Science and Engineering: A., **276** (2000) pp. 108-116.
[4] M.K. Surappa, Aluminium matrix composites: Challenges and opportunities, Sadhana **28** (1), 319-334.
[5]. S.C. Tjong, and Z.Y. Ma Microstructural and mechanical characteristics of in-situ metal matrix composites, Material Science and Engineering: R. **29** (2000) 49-113.
[6] 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, Material Research Bullet-in. **38** (2003) 1387-1392.
[7] P. Colombo, M. Gabriela, and R. Riedel, G. D. Soraru, Polymer-Derived Ceramics: 40 years of research and innovation in advanced ceramics, J. Amer. Ceram. Soc**.,. 93** (2010) pp. 1805-1837.
[8] R. Raj, M. K. Surappa and Sudarshan, United States patent US 8,540,797. (2013) Sep 24.
[9] Sudarshan, K. Terauds, A. R. Anil Chandra, and R. Raj, Polymer-derived in-situ metal matrix composites created by direct injection of liquid polymer into molten magnesium, Metallurgical and Material Transactions: A. **45** (2014) 551-554.
[10] Nagaraj M. Chelliah, Harpreet Singh, Rishi Raj and M.K. Surappa, Processing, microstructural evolution and strength properties of in-situ magnesium matrix composites containing nano-sized polymer derived SiCNO particles, Material Science and Engineering: A. **685** (2017) 429-438.
[11] H. Watanabe, H. Tsutsui, T. Mukai, H. Ishikawa, Y. Okanda, M. Kohzu, K. Higashi, Grain size control of commercial wrought Mg-Al-Zn Alloys utilizing dynamic recrystallization, Material. Transactions, **42** (2001) 1200-1205.
[12]. A. Sanaty-Zadeh, P.K. Rohatgi Comparison between current models for the strength of particulate-reinforced metal matrix nanocomposites with emphasis on consideration of Hall-Petch effect. Material Science and Engineering: A. **531** (2012) 112–118.