Microstructural evolution and strengthening behavior in in-situ magnesium matrix composites fabricated by solidification processing

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Abstract

In-situ magnesium matrix composites with three different matrix materials (including Mg, AZ91 and AE44 Mg-alloys) were fabricated by injecting cross-linked polymer directly into the molten Mg/Mg-alloys, and having it convert to the 2.5 vol% SiCNO ceramic phase using liquid stir-casting method. In-situ chemical reaction took place within the molten slurry tending to produce 42 and 18 vol% Mg₂Si crystals in Mg and AE44 matrix composites, respectively but not in AZ91 matrix composite. Microstructural evolution of Mg₂Si crystals was discussed on the basis of availability of heterogeneous nucleation sites and amount of Al-atoms in the molten slurry. The observed micro-hardness **and yield strengths are** enhanced by factor of four to three as compared to their unreinforced counterparts, and Taylor strengthening was found to be the predominant **strengthening** mechanism in magnesium and AE44 matrix composites. Summation model predicted the yield strengths of the fabricated composites more preciously when compared to Zhang and Chen, and modified Clyne models.

Keywords: *Metal matrix composites (MMCs); In-situ processing; Polymer derived ceramics; Microstructural evolution; Strengthening mechanisms*

1. Introduction

Mg-alloys and Mg-based metal matrix composites (MMCs) have significant potential to design the next generation automotive and aerospace vehicles owing to high specific strength and reduced fuel consumption [1-3]. Solidification processing is the most economical, viable and versatile process to fabricate MMCs for large scale manufacturing sectors. Pradep et al [4] reviewed the important solidification principles underlying the microstructure evolution which governs the composite properties. Surappa [5] investigated particle-solidification front interactions in different MMCs, and concluded that intrinsic material properties as well as processing variables play a major role in controlling the microstructural evolution in the final MMCs. However, solidification processing is not well-suited for the dispersion of fine-sized particles due to chance of producing severe agglomeration by Vanderwals force of attraction, non-uniform particle distribution and poor wettability between ceramic-metal interfaces. Such large and hard agglomerates could be disintegrated by electromagnetic stirring (EMS) and ultrasonic agitation to some extent [6-7].

Ahmed et al [6] justified that EMS results in an elevated shearing force which tends to break away the clustered nano-sized SiC particles and produces an intimate physical contact between nano-sized particles and the melt. Li et al [7] proposed ultrasonic assisted melt processing technique that produces transient cavitations which tend to break up the clustered

fine-sized particles. However, these techniques are more complex and too expensive for commercial exploitation. Most of the technical challenges in solidification processing can be greatly minimized 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. In-situ composites offer superior microstructural/mechanical characteristics as compared to their conventional counterparts. For instance, in-situ MMCs comprised uniform dispersion of fine-sized thermodynamically stable ceramic particles, clean and unoxidized ceramic-metal interfaces along with high interfacial strength, improved hardness/yield strength and elastic modulus. Tjong et al [8] discussed various possibilities of producing in-situ MMCs with different matrix materials and their potential applications. Shamekh et al [9] investigated reaction mechanisms for in-situ AZ91 matrix composites and concluded that intensity of formation of TiC_x - TiB_2 phases increases monotonically with increasing process temperature and time.

Sachin et al [10] applied an ultrasonic vibration to improve the dispersion of in-situ formed Mg_2Si particles in the molten AZ91 composite slurry. Sudarshan et al [11-12] developed a novel processing approach to fabricate in-situ MMCs by utilizing pyrolysis of polymer precursor (polysilazanes) within the molten Mg. Noteworthy feature of this technique is that no chemical reaction between polymer precursor and the host Mg-alloy is required to produce ceramic particles as polymer contains all the constituents of ceramic phases within organic molecules itself.

Recently, N.M. Chelliah et al [13] fabricated magnesium matrix composites containing nano-sized SiCNO ceramic particles using two-stage (casting as well as friction stir processing) method. Further, they also analyzed the strengthening mechanisms and numerical models in two-stage processed composites. However, no attempt has been made to reinforce SiCNO phase or polymer derived ceramic (PDC) particles into commercial Mg-alloys such as AZ91 and AE44 to the best of our knowledge. Sudarshan et al [11] observed that certain degree of chemical reaction between polymer precursor and the host Mg melt results in the formation of Mg_2Si particles at 800 °C. Mg_2Si is considered to be an attractive reinforcing phase owing to its superior mechanical and thermal characteristics to fabricate in-situ Al- Mg_2Si and Mg- Mg_2Si MMCs. However, the presence of coarsened Mg_2Si phase impairs the ductility of the composites.

Zhang et al [14] refined the size of in-situ formed primary Mg_2Si phase by the addition of extra Si particles into molten Al-Mg-Si alloy. Li et al [15] investigated the possibilities of evolving various morphologies in Mg_2Si crystals such as faceted octahedron, hopper octahedron, truncated octahedron and enormous dendrite in Al-Mg-Si alloy. Main objective of the present paper is two-fold: (i) to understand the microstructural evolution in in-situ MMCs dispersed with PDC particles at a temperature of 900 °C and (ii) to investigate their strengthening behavior and validate the numerical models for determining the yield strength of the composites. If Mg_2Si crystal is formed in the final MMCs, it is worthwhile to investigate how the morphology and size of Mg_2Si crystal differ with the matrix

materials as it greatly influences the mechanical properties of the final MMCs.

2. Experimental methods

2.1 Matrix materials and polymer precursor

Commercial purity Mg (99.9%), AZ91 (99.7%) and AE44(99.7%)Mg-alloys are chosen as the matrix materials. **The chemical compositions of reinforced Mg-alloys are provided in Table 1.** Poly(ureamethylvinyl)silazanes (PUVMS) (Ceraset, Kion Corporation), was utilized as a precursor for reinforcement. The precursor in its native liquid form was thermally cross-linked at 400 °C for 5 hours in Argon atmosphere to form a hard epoxy like material. Then organic epoxy was ball milled, yielding solid polymer powder (angular morphology) ranging in size from 1 to 100 µm with a density of 1.0 gcm⁻³. **The chemical composition of as-received and cross-linked PUVMS polymer powder is provided in Table 2.** The weight fraction of polymer precursor to be added into molten Mg/Mg-alloys can be estimated by the following formula [13]:

$$W_f^{precursor} = \frac{\rho_{PDC}}{0.85\rho_{matrix}} V_f^{PDC} \quad (1)$$

The factor of 0.85 indicates the ceramic yield from the cross-linked polymer which was determined experimentally.

2.2 Solidification processing of in-situ MMCs

In-situ MMCs were processed by using a commercially built bottom-poured melting furnace as illustrated in Fig. 1. One kilogram of the machined blocks (matrix material) was melted in a steel crucible using an electrical resistance furnace at a temperature of 700 °C (973 K). The steel crucible was continuously purged with Ar-5%SF₆ gas mixture to eliminate the risk of flammability. **In all the casting experiments, the molten Mg were degassed by Argon (99.999% purity) gas for the period of 10 minutes before the reinforcement.** The melt was then mechanically stirred by a 3-axial stirrer blade at a 600 rpm to create an appropriate vortex field. Subsequently, 3.2 wt% of pre-heated (at a temperature of 473 K) polymer powder was injected into the melt via particle feeder, and mixing was done for 5 minutes. The melt temperature was then increased to 900 °C (1173 K) and stirring process was continued for another 15 minutes to complete the in-situ pyrolysis. Finally, the composite slurries were bottom-poured into a preheated (at a temperature of 473 K) **rectangular split-molds (200 mm length x 150 mm width x 20 mm thickness) made of** plain carbon steel. These solidified composite specimens were designated as PP900-M, PP900-AZ, PP900-AE which were fabricated using pure magnesium, AZ91 and AE44 Mg-alloys as matrix materials, respectively. Here PP refers to polymer powder, and the three digit number 900 refers to pyrolysis temperature of the

casting process. In addition, the castings from unreinforced Mg-alloys and pure magnesium were also fabricated.

3. Material characterization

Optical microscope (Leica DM2700, Germany), scanning electron microscope (JEOL JSM-6610LV, Japan) coupled with energy dispersive spectroscopy (EDS) and **transmission electron microscope (Tecnai T20, FEI Company)** were utilized for microstructural studies. Diffraction spectra of the as-cast composites were collected using an X-Ray Diffractometer (PANalytical X'pert-Pro (MPD), Netherlands). Micro-hardness measurements of as-cast composites were performed using Vicker's micro-hardness testing instrument (Wilson instrument, Model 401/402 MVD UK) at a load of 100 gf for dwell time of 15 s. **All the micro-hardness measurements were performed taking due care to avoid indentation on or near the micro-porous area of the as-cast composites. Uni-axial compression tests were performed using Tinius Olsen mechanical testing machine to record the room temperature mechanical properties at a constant strain rate of 10^{-3} s^{-1} . Cylindrical specimens were machined from the center of as-cast composites by electrical discharge machining (EDM). Compression specimen had a diameter of 4 mm, and 6.5 mm height. Values of reported mechanical properties are average of ten micro-hardness measurements and three compression tests.**

4. Results

Thermogravimetric analysis of cross-linked polymer powder in Argon atmosphere is given in Fig. 2. Typical microstructures of the as-cast pure Mg and PP900-M specimens are shown in Fig.3. PP900-M specimen exhibits significant grain refinement as compared to the pure magnesium (compare Fig. 3(a) and Fig. 3(b)). **Notice that the grain boundaries are not clearly visible in the optical micrographs of the composites owing to segregation of ceramic particles or intermetallics at the grain boundaries. Therefore, we have considered the regime of segregated ceramic particles or discontinuous intermetallics at the grain boundaries having band width of about 5-10 μm as a point of intersection while counting the number of intercepts for grain size evaluation by using a linear intercept method.** The average grain size of this composite is in the range of $40 \pm 10 \mu\text{m}$, while it was $400 \pm 70 \mu\text{m}$ for the case of pure magnesium. As shown in Fig. 3(b), PP900-M specimen is featured by the existence of fine-sized Mg_2Si crystals (dark grey color). Fig. 4 shows the microstructures of AZ91 Mg-alloy and PP900-AZ composite specimens. Both materials typically consist of three phases, namely primary α -Mg, eutectic phase ($\alpha+\beta$), and discontinuous precipitates of β - $\text{Mg}_{12}\text{Al}_{17}$ phase in the vicinity of grain boundaries. The average grain size of these two materials is found to be almost comparable ($\sim 50 \mu\text{m}$). Fig. 5 depicts the microstructures of AE44 Mg-alloy and PP900-AE specimens. The phases in the AE44 Mg-alloy (Fig. 5(a)) are indentified as follows: brighter areas are primary α -Mg and darker areas are Al_xRE_y phase ($x = 2$ or 4 or 11 , $y = 1$ or 3 and RE refers to Ce or La). In Fig 5(a), light grey areas refer to primary α -Mg phase. Similarly,

the phases in PP900-AE specimen (Fig. 5(b)) can be distinguished as follows: light grey particles are Al_xRE_y precipitates, dark particles are Mg_2Si crystals. The average grain size of AE44 Mg-alloy and PP900-AE specimen is measured to be 160 μm and 110 μm respectively. **The amount of porosity (measured by Archimedes's principle) is approximately estimated to be in the range of 1 to 1.5 % in all the as-cast composites.**

Fig. 6(a) illustrates the XRD spectra of as-fabricated in-situ MMCs. It should be kept in mind that the peaks of SiCNO phases have not appeared in diffraction spectra as they are amorphous in nature. It is more obvious that while Mg peaks are observed in all fabricated composites, intermetallic phases of $\beta\text{-Mg}_{17}\text{Al}_{12}$, and Al_xRE_y precipitates are present in PP900-AZ and PP900-AE composites, respectively. The presence of MgO peaks indicates certain degree of oxidation during in-situ processing. XRD spectra confirmed that Mg_2Si phases are present only in the case of PP900-M and PP900-AE specimens; however they are not found in PP900-AZ specimen. Fig. 6(b) depicts the variation of volume fraction of Mg_2Si crystals with amount of Al content (weight percentage) in the Mg melt. It is pertinent to mention that the mean volume fraction of PDC particles in in-situ MMCs having Mg_2Si crystals is found to be always greater than that of projected volume fraction, which was about 2.5%. For instance, mean volume fraction of PDC particles in PP900-M and PP900-AE specimens is estimated to be around 42% and 18%, respectively (see Fig 3(b) and 5(b)). This is primarily associated with the evolution of Mg_2Si crystals, which consume lot of Mg- and Si-atoms from the molten slurry. Fig.7 represents the

microstructural evolution of PP900-M specimen. Fig 7(a) shows that Mg_2Si crystals are characterized by two types of morphologies. First one is dendritic featured Chinese script type (with a particle size of 20-30 μm) and second one resembles platelets or near spherical type particles having a wide range of size distribution, ranging from 1 to 20 μm . The fine-sized platelets (a width of 400 to 500 nm and a length of 1 to 2 μm) are distributed uniformly within each single grain (Fig. 7(b)). Microstructural evolution of solidified PP900-AZ specimen is depicted in Fig. 8. It is evident that $\beta\text{-Mg}_{12}\text{Al}_{17}$ phase is surrounded by supersaturated $\alpha\text{-Mg}$ as well as eutectic phases ($\alpha+\beta$) as seen in Fig 8(a). The noteworthy microstructural feature of PP900-AZ specimen is that most of the SiCNO particles (black color) are entrapped within discontinuous network of $\beta\text{-Mg}_{17}\text{Al}_{12}$ phase at the grain boundaries as observed in Fig. 8(b) and Fig. 8(c). EDS spectra confirmed the presence of Si, C, and O atoms in addition to Mg and Al peaks as depicted in Fig. 8(d). Fig. 9 shows the microstructural evolution of solidified PP900-AE specimen. Fig 9(a) shows the dispersion of Mg_2Si crystals and acicular Al_xRE_y intermetallics in the AE44 matrix composites. Fig 9(b) shows that Mg_2Si crystals represent dendritic morphology with an average particle size of 50-100 μm . The presence of fine-sized intermetallics is also seen in Fig 9(c). Fig 9(d) shows that SiCNO particles (a width of 100 to 200 nm and a length of 0.5 to 1 μm) are distributed homogenously throughout the matrix of the AE44 composites. The detailed analyses of microstructures in Fig. 3(a) through Fig. 5(b) confirm that size and morphology of Mg_2Si crystals vary with the

matrix materials. The micro-hardness data of the fabricated composites is presented in Fig.10. PP900-M composite exhibits highest hardness enhancement of 457%, followed by AE44 composite with an increment of 332.7% and least enhancement of 15% in the case of AZ91 composite as compared to unreinforced counterparts. Fig. 11 depicts the typical compressive true stress-true strain curves of the as-cast in-situ composites. **TEM micrographs of the as-cast magnesium matrix composites taken at different magnifications are shown in Fig 12.** Fig. 13(a) shows the contribution of different strengthening mechanisms to the yield strengths. A comparative analysis of various numerical models to predict yield strength of MMCs is shown in Fig. 13(b).

5. Discussion

5.1 Pyrolysis and its advantages in in-situ MMCs processing

Thermogravimetric analysis of cross-linked polymer gives an idea about the range of temperature where the polymer into ceramic transformation occurs. **In the present study, polymer powder can be converted directly into amorphous SiCNO ceramic phase via pyrolysis mechanism in the temperature range of 800-900 °C (1073-1173 K). When heated to above 1440 °C (1713 K), it is crystallized into mixture of Si₃N₄ and SiC phases [16]. Therefore, the reinforced polymer powder doesn't hold any range of softening point unlike other conventional polymer.** Fig. 2 shows that first weight loss is observed between 280 (553 K) and 550 °C (823 K) because of the evolution of hydrocarbons accompanied by dehydrogenative coupling reactions [17]. The

second weight loss was mainly associated with pyrolysis event which starts nearly at above 600 °C (873 K). During pyrolysis, H-C, Si-H and N-H bonds are broken within the polymer molecules to form covalent bonds between Si, C and N atoms [17]. In the temperature range of 700-800 °C (973-1073 K), the chemical bond between carbon and hydrogen became unstable and hydrogen gas is released [17] **Hydrogen gas escapes directly to free surface of the melt during in-situ pyrolysis of polymer precursor itself.** After the completion of polymer-to-ceramic conversion, the amorphous ceramic phase is constituted by a mixture of various covalent bonds such as Si-C, Si-O, Si-N and C-C [17]. As the final PDC contains certain level of residual oxygen, the general chemical composition of PDC can be represented as $\text{SiC}_x\text{N}_y\text{O}_z$ [13]. Such pyrolysis process was performed within the molten Mg/Mg-alloy in order to fabricate in-situ MMCs. The significant advantage of this in-situ pyrolysis is that evolution of hydrogen gas generates enough pressure which aids in the fragmentation of micron-sized ceramic particles and uniform dispersion of nanoscale ceramic particles throughout the melt. Moreover polymer precursor (PUVMS) are non-toxic; environmentally benign; reasonably stable in ambient atmosphere and exhibit high enough flash points so as not to be a fire hazard. Eroke et al [18] discussed that it is possible to produce amorphous ceramic particles with wide range of silicon oxycarbonitride (SiCNO) chemistries depending on the pyrolysis environment and process temperature. All of these salient features bode well for large scale manufacturing of in-situ MMCs via in-situ pyrolysis of polymer using liquid stir-casting method.

5.2 Microstructural evolution

According to binary Mg-Si system proposed by Yuan et al [19], the maximum solubility of Si-atoms in the Mg melt is very low (0.003 at%) and hence Mg-atoms tend to react with Si-atoms to form Mg_2Si crystal. In the present work, this can happen in two different physical situations; (i) during in-situ pyrolysis at 900 °C (1173 K) and (ii) during solidification below the liquidus temperature of the Mg-alloy. Sunagawa [20] discussed that the surface morphology of evolving crystals is primarily governed by the competition between the intrinsic factors (minimum total surface energy) and the extrinsic factors such as level of impurities, interfacial properties, capillarity, heat/mass transfer and the crystal growth conditions. Li et al [21] predicted that $\{100\}$ faces have the highest growth rate and the preferential growth direction is $\langle 100 \rangle$ tending to form octahedral morphology of Mg_2Si crystal with minimized surface energy. Li et al [15] found experimentally that any perturbation in dominant growth direction $\langle 100 \rangle$ tends to evolve different surface morphologies of Mg_2Si crystal. They also mentioned that when higher concentration of aluminum atoms and impurities suppress the growth rate of the $\langle 100 \rangle$ direction, then the equilibrium shape of Mg_2Si crystal changes into truncated octahedron or even cubic morphology.

5.2.1 Magnesium matrix composite

The grain refinement of PP900-M composite as shown in Fig. 3(b) could be attributed to two primary factors; (i) availability of heterogeneous nucleation sites, and (ii) the restriction of grain growth by PDC particles during solidification. Seetharaman et al [22] reported that uniformly dispersed hybrid nano-B₄C and micro-Ti particles act as nucleation agents and restrict the grain growth. In order to form Mg₂Si crystal, Si-atoms must be first diffused off away from SiCNO particles and this suggests that SiCNO particles could be the most preferential heterogeneous sites for nucleating Mg₂Si crystal as diffusion distance becomes shorter. An in-situ pyrolysis is a highly reactive process accompanied by the evolution of hydrogen gas, which could fragment the pyrolysed SiCNO ceramic particles into nanoscale constituents and disperse them uniformly throughout the melt. The existence of nanoscale SiCNO particles (100-200 nm) had been reported previously by Sudarshan et al [11-12]. The probability of nucleating Mg₂Si crystal is further enhanced owing to high surface/volume ratio of the nanoscale PDC particles. Meanwhile, increase in the number density of PDC particles within the Mg melt suppresses the growth rate in $\langle 100 \rangle$ direction, and then equilibrium crystal shape of Mg₂Si crystal turns into both dendritic as well as platelet-like morphologies. The chemical reaction of forming Mg₂Si crystals can be dictated either by diffusion or kinetic controlled mechanisms and

it is not clear to us presently. In Fig 3(b), the distribution of enormous amount (i.e volume fraction exceeds 0.40) of fine-sized Mg_2Si crystals suggests that nucleation event shall be continued during solidification too. As verified in Fig. 3(b) & Fig. 7(a), the size and morphology of Mg_2Si crystals in PP900-M have two distinct features; coarsened dendritic type and fine-sized platelets as mentioned earlier. **In addition, morphology of few Mg_2Si crystals appears to be spherical in nature as seen in Fig 12(a).** It is quite possible that free Si-atoms which were diffused off away from SiCNO particles may have eventually produced a composition of hyper-eutectic liquid of Mg-8Wt%Si system within the Mg melt. This leads to the nucleation of both primary Mg_2Si dendrites as well as rod-like eutectics of Mg and Mg_2Si crystals. Such microstructural formation in hyper-eutectic liquid of Mg-8wt%Si system was reported by Pan et al [23]. However, the existence of higher convective current within the remaining liquid phase is likely to result in higher chances of breaking up of these rod-like eutectics into fine-sized platelets or spheres and disperse them uniformly throughout the Mg matrix, during solidification.

5.2.2 AZ91 matrix composite

There is no significant grain refinement for the case of PP900-AZ composite as the average grain size is almost comparable with unreinforced matrix material (compare Fig. 4(a) and Fig. 4(b)). This can be ascribed to the absence of Mg_2Si crystals (as verified by XRD spectrum in Fig. 6(a)) which could impede the grain growth of primary α -Mg phase to produce grain

refinement. Further, most of SiCNO particles are entrapped within the β -Mg₁₇Al₁₂ phase (Fig. 8(b)), and hence unable to act as nuclei for grain refinement of primary α -Mg phase. The fundamental reason for not having any Mg₂Si crystals in PP900-AZ composites seems to be as follows. At 900 °C (1173 K), the existence of cluster of Al-atoms in the molten slurry leads to maximize the probability of interrupting the diffusion path for Si-atoms to form Mg₂Si crystals on heterogeneous substrates of SiCNO particles. This explanation is justifiable due to slower diffusion rate of Al-atoms in the Mg solution as reported by Brennan et al [24]. However, Sachin et al, [10] evidenced the formation of in-situ Mg₂Si phase in the molten AZ91 metal after the addition of Si particles under an ultrasonic vibration. Notice that their processing technique is quite different from the present work. For instance, Yang et al [7] mentioned that an ultrasonic vibration can produce transient micro "hot spots" that can have temperature of about 5000 °C (5273 K) and pressure above 1000 atmospheres (101.325 MPa) in the melt. Such a drastic variation in temperature-pressure accelerates the reaction kinetics of Mg₂Si formation as explained by Sachin et al [10]. Moreover, Sachin et al [10] introduced Si particles into the Mg melt by its native powder form which tending to provide an intimate physical contact between Si particles and the Mg melt. However, Si-atoms are introduced in the form of cross-linked polymer in the present work. The chemical reaction between Mg- and Si-atoms is given by the following equation:

(2)

In accordance with thermodynamic model proposed by Yuan et al [19], the estimated Gibbs free energy value for the above chemical reaction is $\Delta G_f^{1173 K} = -69.484 \text{ kJ}$. With this higher negative value in ΔG_f , the chemical reaction should be thermodynamically feasible at 900 °C (1173 K). However, no such chemical reaction occurs and this suggests us that Mg_2Si nucleation is certainly limited either by diffusion or kinetic constraints in the present work. Further, Inem et al [26] also indentified the formation of Mg_2Si phase while reinforcing SiC particles into the molten AZ91 Mg-alloy. They also observed no extensive chemical reaction between Mg and SiC particle at 900 °C (1173 K). However, SiO_2 layer which formed on SiC particles can react with molten Mg to form Mg_2Si phase according to the following chemical reaction mentioned by Inem et al [25]:

However, there is no evidence of forming Mg_2Si phase in the present work and this suggests us that the pyrolysed PDC particles are free from any SiO_2 scale throughout the molten slurry. During solidification, melt is first transformed into primary α -Mg and β - $\text{Mg}_{17}\text{Al}_{12}$ phases. This primary α -Mg phase has certain amount of solubility with Al-atoms depending up on the temperature (maximum solubility of 11.8 at% Al-atoms at 437 °C (710 K) to 1 at% at room temperature). Hence these Al-atoms have a greater tendency to push away any SiCNO particles to the grain boundaries. Once SiCNO particles are rejected out by primary α -Mg phase, there exists a possibility of particle entrapment by β - $\text{Mg}_{17}\text{Al}_{12}$ phase due to geometric

constraints. Hashim et al [26] mentioned that poor wettability between Al melt and SiC particles resulted in grain boundary segregation in Al-based MMCs. Although, SiC and SiCNO particles are chemically distinct, it is reasonable to consider them as equivalent in terms of wettability characteristics with Al-atoms. Further, the existence of supersaturated α -Mg phase (enriched with Al-atoms) and encapsulation of SiCNO particles within β -Mg₁₇Al₁₂ phase provide a positive evidence to support this theory of rejection and entrapment of SiCNO particles by α -Mg and β -Mg₁₇Al₁₂ phases respectively (see Fig. 8(b) and Fig.8 (c)). The formation of Mg₂Si crystals was suppressed as most of the SiCNO particles have been consumed or encapsulated by β -Mg₁₇Al₁₂ phase. In this scenario, Si-atoms from SiCNO particles need to diffuse across the regimes of supersaturated α -Mg and β -Mg₁₇Al₁₂ phases and it is not physically feasible during solidification. Hence the possibility of forming Mg₂Si crystal in PP900-AZ composite could be ruled out.

5.2.3 AE44 matrix composite

During in-situ pyrolysis, the chance of forming Mg₂Si crystals seems to be limited again for the same reasons mentioned earlier for PP900-AZ composite, i.e the existence of excessive Al-atoms in the molten slurry does not favor any nucleation event for producing Mg₂Si crystal. However, during solidification, the surrounding medium for nucleating Mg₂Si crystals is completely different. Here, the liquid phase was converted in to

primary α -Mg phase and Al_xRE_y phase. Most of the Al-atoms are expected to bind with RE elements in the Mg melt to form an acicular Al_xRE_y precipitates. Chen et al, [27] found that RE additions have positive influences on the nucleation of Mg_2Si crystals in Al-Mg-Si alloys. Hence, the most preferential sites for nucleating Mg_2Si crystals could be the Al_xRE_y precipitates. Once Mg_2Si crystal is nucleated, and it persists its growth along the preferential growth direction $\langle 100 \rangle$ to form an equilibrium crystal shape of octahedron morphologies. However, the existence of SiCNO particles in the surrounding medium (Fig 9(d)) may impose constraint to this equilibrium growth direction, and eventually results in the formation of dendritic Mg_2Si crystals as shown in Fig. 9(b).

It is worthwhile to correlate the volume fraction of Mg_2Si crystals in the final composites with the amount of Al-atoms present in the molten slurry. As shown in Fig. 6, it can be seen that if the weight percentage of Al-atoms approaches 9 wt% as like in the case of AZ91 matrix composite, then the chance of forming Mg_2Si crystal was suppressed completely. Higher concentration (9 wt%) of Al-atoms and slower diffusion rate of Al-atoms within the molten slurry seem to be the major reason behind the suppression of Mg_2Si formation for AZ91 matrix composite. Further, this graph also suggests us that when the weight percentage of Al-atoms changes from 0 wt% to 4 wt%, then the morphology of Mg_2Si crystal predominantly transforms from fine-sized platelets into coarsened dendritic type.

5.3 Strengthening behavior

5.3.1 Contribution of strengthening mechanisms

Hardness property of the composites is of significant importance for any wear resistant applications. The observed significant improvement in hardness for PP900-M and PP900-AE composites is mainly associated with the contribution of different strengthening mechanisms as seen in Fig.10. However, there is only marginal increment in the hardness of PP900-AZ composite as compared to the unreinforced AZ91 Mg-alloy. The possibility of impeding the movement of dislocation within the primary α -Mg phase seems to be futile as most of the SiCNO particles are entrapped within discontinuous network of β -Mg₁₇Al₁₂ phase (Fig 8(b)). Nevertheless, PP900-AZ composite is expected to have high temperature creep resistance as β -Mg₁₇Al₁₂ phase is dispersed with thermally stable SiCNO particles. The hardness (HV) of the composites can be converted into yield strength (σ_y) using an empirical relation proposed by Sanders et al [30] as follows:

$$\sigma_y \approx \frac{HV}{2.8} \quad (3)$$

The compressive yield strengths of as-cast in-situ composites along with unreinforced Mg-alloys were determined from yield point at which strain-strain curves becomes non-linear as seen in Fig. 11. Notice that yield strengths determined by hardness tests are almost matched with yield strength values measured from compression test data.

Mabuchi and Higashi [28] studied the influence of various strengthening mechanisms in Mg-Si alloys. Tjong [29] investigated the role of different strengthening mechanisms for enhanced mechanical properties of nano-particle reinforced MMCs. The summary of such different strengthening models is provided in Table 3 [13]. The properties and parameters which are used for calculating the various strengthening modes are provided in Table. 4 and Table. 5.

As seen in Fig 13(a), it can be seen that the contribution of Taylor strengthening is enormous in case of both the PP900-M and PP900-AE specimens when compared to other strengthening mechanisms. When a composite is imposed to change in temperature, the differences in coefficients of thermal expansion (CTE) between matrix material and reinforced particles shall produce a thermal strain and internal stress state changes. In order to accommodate this thermal mismatch effect, dislocations are generated around reinforced particles within the matrix material so as to reduce the stored energy. The magnitude of thermal strain ($\Delta\epsilon_T = \Delta\alpha\Delta T$) determines the density of dislocations generated within the composites. Notice that all of the fabricated MMCs were subjected to temperature difference (ΔT) of about 873 K. Further, the CTE difference between the Mg matrix and SiCNO particles is $\Delta\alpha = 23 \times 10^{-6} (K^{-1})$ while the Mg matrix experiences CTE mismatch of $19 \times 10^{-6} (K^{-1})$ with Mg_2Si crystals. Therefore, the probability of achieving highest density of dislocations (in range of about 10^{14} - 10^{15}) increases steadily with fabricated composites

owing to larger thermal strain induced during stir-casting process. **As observed in Fig. 12(b) and 12(c), the existence of large number of dislocations in the as-cast magnesium matrix composites confirms the predominance of Taylor strengthening.** Higher the density of dislocations in the composites, lesser the mean free path travelled by a moving dislocation which eventually tending to enhance the contribution of Taylor strengthening.

In order to validate this above hypothesis, some of the PP900-M and PP900-AE specimens were subjected to annealing treatment at a temperature of 100 °C (373 K) for 24 hours followed by a slow cooling in order to annihilate the majority of dislocations which were generated during stir-casting process. As expected, these annealed composites show significant reduction in their yield strengths (337 MPa for annealed PP900-M and 510 MPa for annealed PP900-AE specimens) when compared to as-cast counterparts (629.5 MPa for as-cast PP900-M and 891.07 MPa for as-cast PP900-AE specimens). Further, it can be noticed that the intensity of Taylor strengthening is much higher in PP900-AE when compared to PP900-M specimen. This difference in Taylor strengthening can be associated with existence of hybrid particles which include both the fine-sized SiCNO and coarsened Mg_2Si phases in PP900-AE composite. On the other hand, the matrix of PP900-M composite contains mainly of fine-sized Mg_2Si platelets as almost all of the SiCNO particles were consumed during chemical reaction. Further, there occurs a disparity in the generation of geometrically necessary dislocations (GNDs) among these two composites during plastic deformation.

GND is an another important local relaxation mechanism in composites by which dislocations are generated close to the ceramic particles in order to accommodate the mismatch of plastic deformation with the matrix material due to difference in elastic modulus. However, the tendency towards the generation of GNDs decreases with PP900-M specimen as its matrix material contains nearly about 50 vol% of the PDC particles. It is justifiable that PP900-M specimen can behave almost like isotropic composites microscopically experiencing isothermal strain and least degree of plastic deformation mismatch. Further, the addition of GNDs component over estimates the Taylor effect too. Therefore, the GNDs component can be neglected in Taylor strengthening for PP900-M specimen. For PP900-AZ specimen, thermal mismatch effect loses its importance in first place. This can be associated with the entrapment of SiCNO particles by β -Mg₁₇Al₁₂ phase, which in turn generates least amount of dislocations within the primary α -Mg phase which eventually leads to a lowest Taylor strengthening as seen in Fig 13(a).

Next to Taylor strengthening, the load transfer strengthening also plays a major role in enhancing the yield strengths of the fabricated composites. This is mainly associated with load bearing effect of hard ceramic phase due to presence of higher volume fraction of reinforced PDC particles (i.e $V_f \approx 0.42$ for PP900-M and 0.28 for PP900-AE specimen). Sudarshan et al [11-12] reported that in-situ pyrolysis of polymer within molten Mg results in the uniform dispersion of fine-sized ceramic particles. Therefore, the

Orowan strengthening should be taken into consideration in order to predict the yield strength of composites as mentioned by Zhang and Chen et al [31]. The Orowan strength is mainly determined by dispersed particles being able to impede the movement of dislocation and Orowan strength inversely scales with the mean inter-particle spacing between the dispersed particles. Therefore, the intensity of trapping the dislocations by ceramic particles (i.e contribution of Orowan strengthening) increases with decreasing the particle size and increasing the volume fraction of the PDC particles. In Fig 13(a), it can be seen that the relative contribution of Orowan strengthening in PP900-M specimen is increased by 4.92 times in comparison with that of PP900-AZ specimen and enhanced by 1.80 times as compared to PP900-AE specimen. This can be attributed to a rise in the volume fraction of fine-sized ceramic particles for PP900-M specimen. As mentioned earlier, there occurs a significant grain size refinement for PP900-M specimen as compared to PP900-AZ and PP900-AE specimens (see Fig 3(a) through Fig 5(b)). 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. Therefore, it can be expected that PP900-M composite experiences highest enhancement in Hall-Petch strength of 27.7 MPa, followed by AE44 composites with an increment of 2.89 MPa and least enhancement of 0.85 MPa for the case of AZ91 matrix composite as shown in Fig 13(a).

5.3.2 Verification of the numerical models

The most common numerical models to predict the yield strength of particulate MMCs are as follows [13, 32]: (i) the simple summation model which adds up all the strengthening contributions by assuming that each mechanism behaves individually (ii) Zhang and Chen model is a modified version of shear-lag model which considers the effects of Orowan, Taylor and load transfer strengthening but neglects the effect of Hall-Petch strengthening and (iii) modified Clyne model includes the effects of all strengthening mechanisms which act unevenly throughout the matrix by least-square approximation. Sanaty-Zadeh et al [32] reported that the modified Clyne method can predict the yield strength more precisely than any other methods after comparing the various numerical models for the particulate MMCs. The governing equations for these numerical models are provided in Table 6. As seen from the Fig 13(b), both the Zhang and Cheng and the modified Clyne models over estimate the yield strength of PP900-M and PP900-AE specimen except the case of PP900-AZ specimen. On the other hand, the agreement between yield strength of composites predicted by summation model and experimental methods seems to be good (Fig 13(b)). The discrepancy between these two numerical models and the experimental results stems from the following: Zhang and Cheng and the modified Clyne models assume that no strengthening mechanism can act individually and should be inter-dependent. Further, the variation in particle size distribution and the existence of hybrid ceramic particles were not considered by Zhang and Chen and modified Clyne models. Therefore, these

two numerical models seem to be more valid in particulate MMCs exhibiting uni-modal particle size distribution and uniform dispersion of mono-phase ceramic particles. Kunkun et al [33] proposed a numerical model to calculate the yield strength of bimodal particle reinforced AZ91-based MMCs which is quite different from both the Zhang and Chen and the modified Clyne models. In other words, these two numerical models lose their precision if bi-modal particle size distribution exists in particulate MMCs. Therefore, the variation in particle size distribution and the existence of hybrid polymer derived ceramic particles (Mg_2Si and SiCNO phases) are found to be some of the important experimental factors leading to deviation in the yield strength values predicted by Zhang and Chen as well as modified Clyne models. As mentioned earlier, summation model predicts the yield strengths more precisely close to the experimental values. Thus, it is evident clearly that each strengthening mechanism acts individually in the fabricated composites.

In summary, we may emphasize that in-situ pyrolysis approach opens an opportunity window for the material researchers to develop futuristic Mg-based hybrid in-situ MMCs due to the formation of in-situ SiCNO and Mg_2Si phases. Furthermore, in-situ pyrolysis produces a wide range of particle size, and morphologies of PDC particles, so that one can tailor the mechanical properties for specific engineering requirements. Notice that ductility of the composites can be also enhanced either by reducing the volume fraction of Mg_2Si crystals or by controlling the size and morphologies of Mg_2Si crystals. This can be achieved via optimization of

in-situ processing variables such as pyrolysis temperature, pyrolysis time, and cooling rate. We also strongly believe that rapid solidification technique minimizes the formation of coarsened dendritic Mg_2Si crystals during solidification processing [34].

6. Conclusion

1. In-situ magnesium matrix composites were fabricated successfully by injecting cross-linked polymer powder directly into, and having it convert to the SiCNO ceramic phase, within molten Mg/Mg-alloy using liquid stir-casting method.
2. Most of the SiCNO particles were entrapped within discontinuous network of $\beta\text{-Mg}_{17}\text{Al}_{12}$ intermetallic phase near the grain boundary regime in AZ91 matrix composite. This was associated with rejection and entrapment of SiCNO particles by $\alpha\text{-Mg}$ and $\beta\text{-Mg}_{17}\text{Al}_{12}$ phases, respectively.
3. In-situ Mg_2Si crystals were also formed in magnesium and AE44 matrix composites due to chemical reaction within molten slurries, but were not formed in AZ91 matrix composite. Higher concentration and slower inter-diffusion rate of Al-atoms within molten slurry suppressed the formation of Mg_2Si crystals for AZ91 matrix composite.
4. The transition in size and morphologies of Mg_2Si crystals are primarily governed by the matrix composition, nature of heterogeneous nucleation sites and amount of Al-atoms within molten slurries.

5. Magnesium matrix composite exhibited a highest hardness **or yield strength** enhancement of 457%, followed by AE44 matrix composite with an increment of 333% and least enhancement of 15% for AZ91 matrix composite as compared to their unreinforced counterparts. This was attributed to the contribution of different strengthening modes such as Taylor, load transfer, Orowan, and Hall-Petch effects with Taylor as the most dominant strengthening mechanism.

6. Summation model fits well with experimental yield strength values of the fabricated composites as compared to Zhang and Chen, and modified Cylne models. This can be ascribed to variation in particle size distribution and the existence of hybrid polymer derived ceramic particles (Mg_2Si and SiCNO phases) in the composites.

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Appendix (Notations) :

The following symbols are used in the present paper:

$W_f^{precursor}$	Weight fraction of polymer powder
V_f^{PDC}	Projected volume fraction of PDC particles
ρ_{PDC}	Theoretical density of PDC particles
ρ_{matrix}	Theoretical density of matrix material
D_f	Mean grain size of the final matrix
D_0	Mean grain size of the original matrix
$\Delta\sigma_{HP}$	Enhancement in yield strength by Hall-Petch effect
K_{HP}	Hall-Petch coefficient
$\Delta\sigma_{OR}$	Enhancement in yield strength by Orowan effect
β	Numerical constant
G_m	Shear modulus of the matrix
b	Burger vector of the matrix,
d_p	Mean diameter of the reinforced particles
V_f	Volume fraction of the reinforced particles
λ	Mean inter-particle spacing between particles
ν_m	Poisson ratio of the matrix material

$\Delta\sigma_{LT}$	Enhancement in yield strength by load bearing effect
σ_{ym}	Yield strength of the original matrix
$\Delta\sigma_{Taylor}$	Enhancement in yield strength by Taylor effect
φ	Taylor factor
$\Delta\alpha$	Thermal mismatch difference between matrix and reinforcement
ΔT	Temperature difference between process and test
ε_p	Plastic strain
$\Delta\sigma_S$	Enhancement in yield strength by summation
$\Delta\sigma_{ZC}$	Enhancement in yield strength by Zhang and Chen model
$\Delta\sigma_{MC}$	Enhancement in yield strength by modified Clyne model

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Table 1: Chemical composition of the AZ91 and AE44 Mg-alloys

M atrix		Chemical composition (wt %)							
	Al	RE (Ce, La) Misch metal	Zn	Mn	Si (Max)	Fe (Max)	Cu	Ni	Mg
AZ91C	8.3-9.7	-	.3-1.0	.15-5.0	.1	.005	.03	.002	Balance
AE44	3.6-4.8	3.8-5.1	.01	.3	.01	.005	.03	.002	Balance

Table 2: Chemical composition for starting and cross-linked Poly PUVMS precursor materials

Material	Composition (wt%)				
	Si	C	N	O	H
PUVMS	43.9	27.3	19.1	0.38	8.1
Cross-linked @ 773 K, in Ar	44.1	28.5	19.7	0.59	6.9

Table 3: Summary of various strengthening mechanisms in MMCs [13, 29]

Strength ening models	Mechanisms	Governing equations
Hall- Petch	Interaction of dislocations at the grain boundaries	$\Delta\sigma_{HP} = K_{HP} [D_f^{-1/2} - D_o^{-1/2}]$
Orowan	Interaction of dislocation with reinforced particles	$\Delta\sigma_{Orowan} =$ $\beta \frac{0.4G_m b}{\pi\lambda} \left[\frac{\ln\left(\frac{d_p}{b}\right)}{(1-\nu_m)^{1/2}} \right]$ $\lambda = d_p \left[\sqrt{\frac{\pi}{4V_f}} - 1 \right]$

Taylor	Dislocation enrichment due to thermal mismatch between matrix and reinforced particles	$\Delta\sigma_{Taylor} = \sqrt{3}\phi G_m b \left[\frac{12V_f \Delta\alpha \Delta T}{b(1-V_f)d_p} + \frac{8V_f \varepsilon_p}{bd_f} \right]^{1/2}$
Load bearing	Load transfer from soft matrix to hard particles	$\Delta\sigma_{LT} = \frac{1}{2}\sigma_{ym}V_f$

Table 4: Material properties and parameters of the investigated materials

Properties	Matrix		
	Mg	AZ91	AE44
Average grain size of unreinforced Mg-alloys, μm	400.0	54.6	160

Hall-Petch Coefficient, $\text{MPa}\cdot\text{m}^{-2}$	0.280	0.130	0.17 8
Yield strength, MPa	113	288	206
Shear modulus, GPa	16.5		
Poisson ratio	0.35		
Burger vector, nm	0.32		
Thermal expansion coefficient, μK^{-1}	26.5		
Process Temperature, K	1173		
Test Temperature, K	300		

Table 5: Important parameters of the fabricated composites

	Magne sium matrix composites	AZ91 matrix composites	AE44 matrix composites
Average grain size, μm	45	50	110
Volume	–	0.05	0.10

fraction of SiCNO			
Volume fraction of Mg ₂ Si crystals	0.42	0.0	0.18
Particle size of SiCNO, nm	-	150	140
Particle size of Mg ₂ Si crystals, μm	0.450	-	40-45

Table 6: Governing equation for different numerical models to predict the yield strength of MMCs [13,32]

1	Numerical models	Equations

Summation	$\Delta\sigma_S = \sigma_{ym} + \Delta\sigma_{Taylor} + \Delta\sigma_{LT} + \Delta\sigma_{Orowan} + \Delta\sigma_{HP}$
Zhang and Chen	$\Delta\sigma_{ZC} = (1 + 0.5V_f) \left[\sigma_{ym} + \Delta\sigma_{Orowan} + \Delta\sigma_{Taylor} + \left(\frac{\Delta\sigma_{Orowan}\Delta\sigma_{Taylor}}{\sigma_{ym}} \right) \right]$
Modified Clyne	$\Delta\sigma_{MC} = \sigma_{ym} + \sqrt{(\Delta\sigma_{Taylor})^2 + (\Delta\sigma_{LT})^2 + (\Delta\sigma_{Orowan})^2 + (\Delta\sigma_{HP})^2}$