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Chapter

Solidification Processing of Magnesium Based In-Situ Metal Matrix Composites by Precursor Approach

Nagaraj Chelliah Machavallavan, Rishi Raj and M.K. Surappa

Abstract

In-situ magnesium based metal matrix composites (MMCs) belong to the category of advanced light weight metallic composites by which ceramic dispersoids are produced by a chemical reaction within the metal matrix itself. In-situ MMCs comprised uniform distribution of thermodynamically stable ceramic dispersoids, clean and unoxidized ceramic-metal interfaces having high interfacial strength. In last two decades, investigators have been collaborating to explore the possibility of enhancing the high temperature creep resistance performance in polymer-derived metal matrix composites (P-MMCs) by utilizing polymer precursor approach. A unique feature of the P-MMC process is that since all constituents of the ceramic phase are built into the polymer molecules itself, there is no need for a separate chemical reaction between the host metal and polymer precursor in order to form in-situ ceramic particles within the molten metal. Among the different polymer precursors commercially available in the market, the silicon-based polymers convert into the ceramic phase in the temperature range of 800–1000°C. Therefore, these Si-based polymers can be infused into molten Mg or Mg-alloys easily by simple stir-casting method. This chapter mainly focuses on understanding the structure–property correlation in both the Mg-based and Mg-alloy based in-situ P-MMCs fabricated by solidification processing via polymer precursor approach.

Keywords: in-situ metal matrix composites, magnesium, Mg-alloys, solidification, polymer derived ceramics

1. Introduction

In-situ metal matrix composites offer superior microstructural/mechanical characteristics compared to their conventional counterparts. In-situ MMCs are characterized by uniform dispersion of fine-sized thermodynamically stable ceramic particles, clean and unoxidized ceramic-metal interfaces having high interfacial strength, improved hardness/yield strength and elastic modulus [1]; In-situ composite fabrication techniques are gaining attraction among the researchers since this techniques overcome several processing related issues such as non-uniformity of particle

distribution, poor wettability and weak interfaces associated with composites produced by conventional processing techniques [2–3]. In-situ processing methods use a chemical reaction between liquid–gas, liquid–liquid, liquid–solid, and mixed salts to generate fine ceramic particles in the metal matrix. For instance, silicon, dissolved in copper, may be converted into a dispersion of silica particles by reacting with oxygen diffusing in from the environment [4]. Enormous data are available in the composite literature regarding the processing of Al-based in-situ composites whereas data on in-situ Mg-based composites seems to be very limited [5–6].

In last two decades, investigators have been collaborating to enhance the high temperature creep resistance of metal matrix composites by utilizing polymer precursor approach [7–19]. A noteworthy feature of this polymer precursor approach is that no chemical reaction between polymer precursor and the host Mg is required to produce in-situ ceramic particles because the polymer contains the constituents of ceramic phases within organic molecules itself [14–15]. The pyrolysis is a highly reactive process, accompanied by the evolution of hydrogen, which disperses the ceramic phase into nanoscale or sub-micron constituents [1]. However, the two critical main issues were identified in earlier work [14–15] 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°C. These brittle Mg_2Si ceramic phase significantly reduce the ductility of fabricated composite. In addition, formation of Mg_2Si phase leads to reduction in the amount of polymer precursor available for in-situ generation of sub-micron or nano-sized SiCNO particles, and (ii) most of the PDC particles are pushed away by the solidification front and get segregated at the grain boundaries. Such grain boundary segregation limits any enhancement in the mechanical properties of the final in-situ MMCs. These two critical issues can be mitigated by adopting the following research methodologies [13] namely (i) The intensity of Mg_2Si formation can be minimized by lowering the pyrolysis temperature from 800 to 700°C. (ii) The issue of grain boundary segregation can be reduced by adopting friction stir processing (FSP) treatment. 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 [1].

The microstructural design of light weight MMCs for creep resistant applications involves the uniform dispersion of thermally stable nano-scale ceramic particles throughout the grain matrix [1]. The potential for incorporating nano-sized PDC particles into a light weight metal is made possible by polymer precursor approach [1]. The direct injection of liquid polysilazane precursor into molten metal and the subsequent casting process seems to be most advantageous and viable route of producing P-MMCs. If nano-scale particles of PDCs are dispersed uniformly in the magnesium matrix, it can be expected to impede dislocation motion and resist coarsening at high temperatures, thereby holding the promise of a new genre of light weight polymer-derived P-MMCs [1]. Therefore, the present chapter mainly focuses on understanding the correlation between structure-properties of in-situ magnesium matrix composites containing SiCNO particles via polymer precursor approach.

2. In-situ polymer precursor approach

Rishi Raj and M. K. Surappa jointly [14] patented a novel pyrolysis infiltration process (PIP) to fabricate Mg-based P-MMCs using liquid metallurgical route. The PIP process has great generality because different organic precursors for producing oxide, carbides, nitrides, and borides are commercially available as indicated in **Table 1** [1].

Polymer precursors	Ceramic phases	Merits	Demerits
Polysilazanes	Si-C-N-O (amorphous)	Commercially available Mostly air tolerant Can be thermally cross–linked	Can form silicides
Siloxanes	Si-C-O (amorphous)	High molecular weight Environmentally benign Pyrolyzes at 700–1000°C	
Carbosilanes	Si-C (crystalline)		
Alkoxides	Metal oxides, e.g. SiO_2, ZrO_2, HfO_2, Al_2O_3 etc.	Commercially available Moderately air tolerant. Pyrolyzes at 400°C	Cannot be cross–linked High vapor pressure

Table 1.
Types of organic precursors that can serve as a source for ceramics in MMCs [1, 15].

Also, the process would permit the addition of the desired volume fractions of the ceramic enabling the nanostructural design, and production of P-MMCs with a wide range of mechanical properties, meant especially for high temperature creep resistant applications [1]. When the melting point of a metal lies below 800°C, the Si-based polymer can be added into the molten metal by a stir-casting method. Magnesium and aluminum matrix composites are typical examples for this PIP approach. The conversion of the polymer into the ceramic phase releases hydrogen and small amounts of hydrocarbons. During in-situ processing these gaseous species must migrate to the free surface in a way to avoid any porosity in the final castings. This can be an issue in aluminum composite castings; although it does not appear to constrain the production of magnesium composite castings. Originally, the standard procedure recommended by inventor of this PIP process [14] is to add the cross-linked polymer powder just above the melting point and then superheat the metal to 800°C to convert the organic into the ceramic phase. Later, they realized that direct injection of the liquid polymer is even most simpler [15], and holds greater potential for futuristic development of polymer derived metal matrix composites (P-MMCs).

Figure 1 depicts the schematic diagram of casting setup used to fabricate in-situ Mg/Mg-alloys based P-MMCs [1]. The systematic procedures for composite fabrication can be described in the following steps; [1].

i. Firstly, one kilogram of Mg blocks (Pure Mg or Mg-alloys (AZ91 and AE44 series) was melted in a steel crucible using an electrical resistance furnace at a temperature range of 700–900°C.

ii. In order to eliminate the flammability and risk of fire hazards with molten Mg, the steel crucible was then continuously purged with Ar-5%SF6 gas mixture.

iii. The molten Mg was degassed by argon (99.999% purity) gas for the period of about 10 minutes before reinforcement. The composites are reinforced with a projected volume fraction of 2.5% of PDC particles during stir-casting process.

iv. The melt was mechanically stirred by a 3-axial stirrer blade at 600 rpm to create a good vortex in the melt. Subsequently, required amount of liquid polymer or cross-linked polymer (pre-heated at a temperature of 200°C) was injected into the melt and the stirring was continued for next 15 minutes in order to ensure completion of in-situ pyrolysis.

v. The polymer to ceramic conversion of cross-linked polymer occurs in single stage (pyrolysis) whereas the liquid polymer conversion takes place in two stages (both cross-linking as well as pyrolysis).

vi. In the temperature range of 700–800°C, the bonds between carbon and hydrogen in polysilazane precursor become unstable and hydrogen gas is released. These dangling carbon atoms self-assemble into graphene-like network or retained as free carbon clusters [20].

vii. 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 [20]. As the final PDC contains some of residual oxygen, the general chemical composition of PDC can be expressed as SiCNO.

viii. After processing, the mixed molten slurry was bottom-poured into a pre-heated split-molds made of steel.

The designation of these fabricated Mg matrix composites has been indexed as PP700, PP800, PL700, and PL800. Mg-alloys based P-MMCs were designated as PP900-AZ, and PP900-AE which were fabricated using AZ91 and AE44 Mg-alloys as matrix materials, respectively. Here, PP refers to polymer derived composites made using cross-linked powder, and PL indicates polymer derived composites made using as-received liquid ceraset. The last 3 digits refer to process or pyrolysis temperature. In addition, the castings from pure magnesium, and unreinforced Mg-alloys were also fabricated using similar processing parameters.
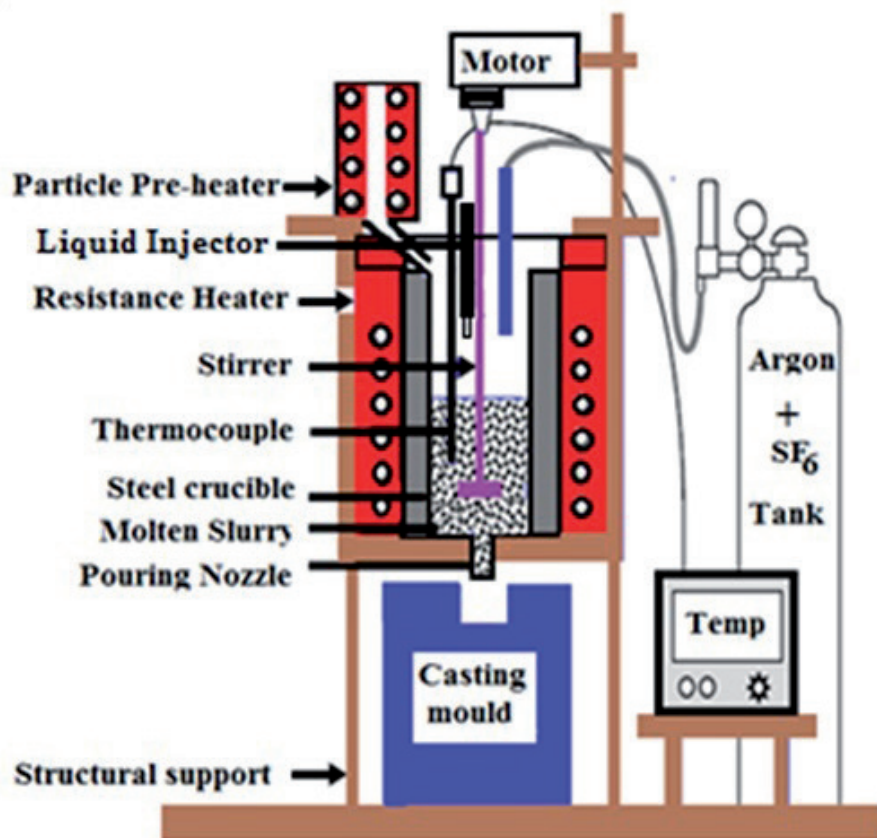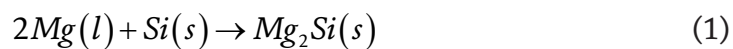

Figure 1.
*Schematic diagram of stir-casting furnace used for fabricating in-situ composites [1].*

3. Structure-property correlation of as-cast In-situ Mg-based metal matrix composites

### 3.1 Microstructural characteristics

Figure 2 shows the microstructural evolution of as-cast magnesium composites fabricated under four different processing conditions. It is clearly evident from microstructural analysis that the as-cast PP800/PL800 specimen exhibit bi-modal grain size distribution, whereas the as-cast PP700/PL700 specimen represents more or less uni-modal grain size distribution. Such difference in microstructural characteristics arises because of the fact that higher amount of heterogeneous nucleation sites is available for producing Mg crystals in PP800/PL800 specimen as they contain both the SiCNO and Mg2Si particles. However, it is mostly SiCNO particles with negligible amount of Mg2Si particles are observed for the case of PP700/PL700 specimen. This could be also easily inferred from XRD spectra (**Figure 3**). For instance, the intensity of Mg_2Si peaks appears to be stronger in composites processed at temperature of 800°C and weak in composites processed at 700°C. Notice the fact that since SiCNO ceramic phases are amorphous in nature, corresponding peaks have not appeared in diffraction spectra. Most importantly, it is also observed that the peaks of SiO_2 and $Mg(SiO_4)$ phases are apparent only in the as-cast PL700/PP700 specimen, however, but such peaks are absent in as-cast PL800/PP800 specimen. It is likely expected that because of lower solubility of Si-atoms in the molten magnesium, the chemical reaction takes place between the magnesium and silicon to form Mg_2Si crystal according to the following equation [21]:

$$2Mg(l) + Si(s) \rightarrow Mg_2Si(s) \tag{1}$$

According to the chemical reaction (1), it can be estimated that the change in Gibbs free energy values (ΔG_f) are found to be −63.578 kJ and −57.926 kJ for the
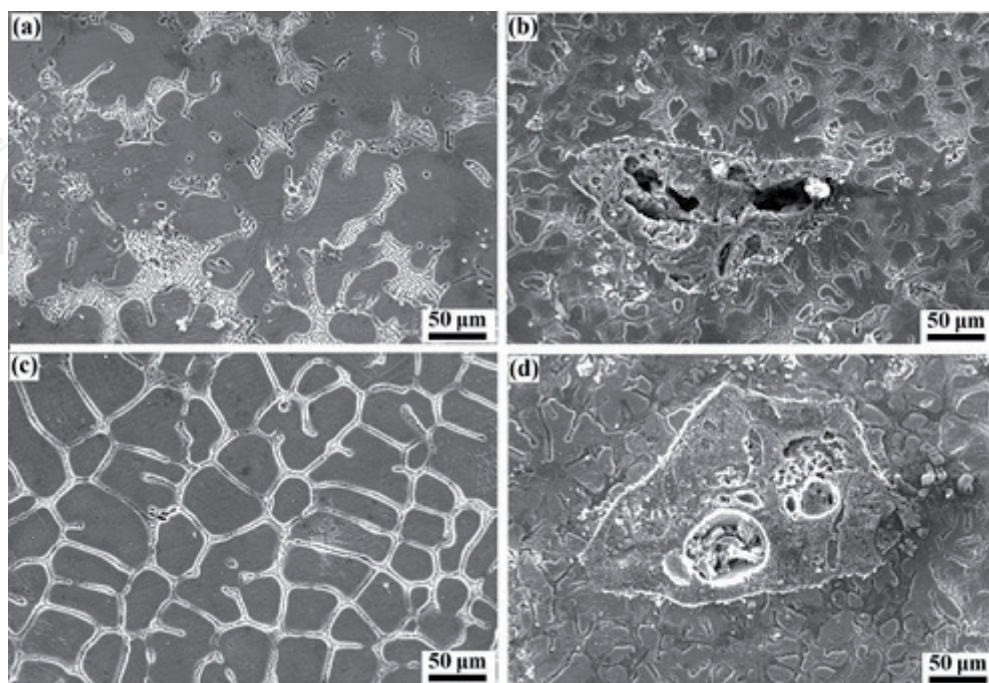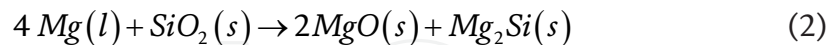

Figure 2.
Microstructural evolution of in-situ Mg matrix composites in as-cast condition (a) PP700 composite (b) PP800 composite (c) PL700 composite and (d) PL800 composite [1].
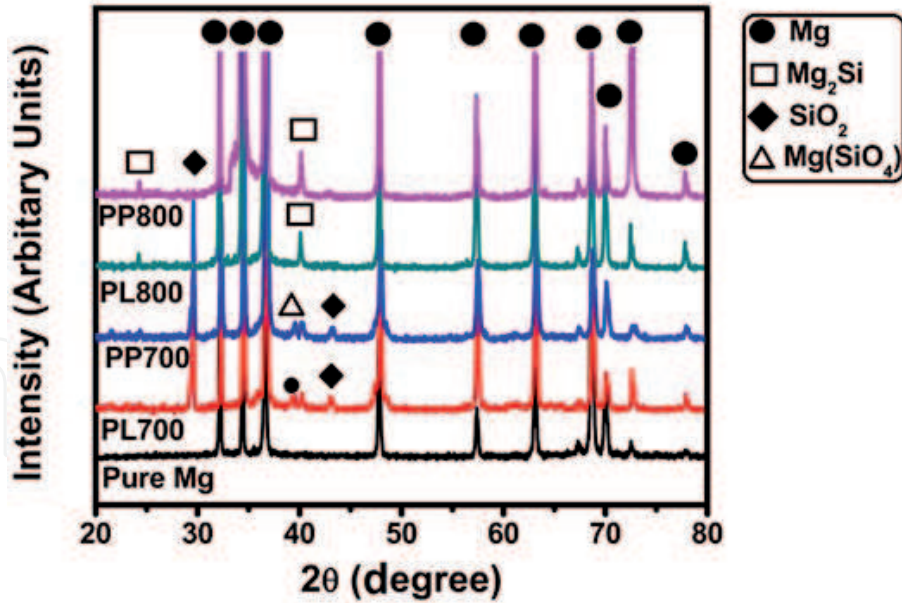
Figure 3.
XRD spectra of pure Mg and in-situ Mg matrix composites [1].

processing temperatures of 800°C and 700°C, respectively. The higher negative value at ΔG_f at 800°C represents that the tendency for Mg$_2$Si formation is increased by increasing the pyrolysis temperature from 700 to 800°C. In other words, it is possible to minimize the formation of Mg$_2$Si phase by reducing the processing temperature from 800 to 700°C during in-situ pyrolysis of the polymer precursor.

Inem et al. [22] reported that there is no extensive direct chemical reaction occurs between Mg and SiC particle to form Mg$_2$Si crystal at 900°C in the SiCp particles reinforced AZ91 Mg-alloy. However, they predicted that SiO$_2$ scale that forms on SiC particle can react with molten Mg to form Mg$_2$Si according to the following chemical reaction;

$$4\,Mg(l) + SiO_2(s) \rightarrow 2MgO(s) + Mg_2Si(s) \tag{2}$$

This data indicates that some amount of SiO$_2$ scale must be always present in order to produce any Mg$_2$Si phase in the composite. As it can be seen in **Figure 3**, XRD data shows the presence of SiO$_2$ peaks only in the PL700 specimen but not in the as-cast PL800 specimen. This means that the PL800 specimen consumes SiO$_2$ phase completely to form Mg$_2$Si crystal whereas some free SiO$_2$ is left behind in the PL700 specimen due to lack of formation of Mg$_2$Si particles.

According to constitutional supercooling theory, the ratio of temperature gradient (G) to growth rate (R) determines the grain morphology of the final castings during solidification [23]. This theory predicts that the microstructures can be changed from cellular to columnar dendritic, and then to equiaxed dendritic morphology if the solidification condition possess low G/R ratio [23]. It is worthwhile to mention the fact that constitutional supercooling theory can also be applied to the solidification of metal matrix composites if the tip of the solidification front contains certain level of solute impurities. Kim et al. [24] pointed out that any change in the direction of heat flux resulting in different microstructures during solidification of the metal matrix composites. They explained that if the direction of heat flux is same to that of crystal growth, then equiaxial dendritic

growth occurs under solidification condition. On the contrary, columnar growth occurs in the final castings if the directions of heat flux and crystal growth are different or antiparallel. The second scenario is quiet possible if heat transfer occurs by conduction mechanism across the mold material. This means that positive temperature gradient exists in front of the solidification front for columnar microstructures and negative temperature gradient for the case of dendritic grain microstructures. We believed that the presence of Mg_2Si particles at 800°C in the molten magnesium act as an effective heterogeneous nucleation site to produce equiaxial dendritic grain simultaneously throughout the molten magnesium. However, any absence of Mg_2Si particles in the molten magnesium fabricated at 700°C leads to produce columnar grain from the edge to center of the mold. Therefore, the microstructures of the final in-situ magnesium composites should be different as they were processed under two different solidification conditions. As shown in **Figure 2**, the microstructures of PP700/PL700 composites show more or less columnar grain morphology while the grain morphology of PP800/PL800 composites appears to be predominantly dendritic in nature. From experimental observation, it can be understood clearly that the grain morphology in the final castings can be controlled by imposing variation in G/R ratio and heat flux direction by changing the process or pyrolysis temperature of the in-situ magnesium composites.

Figure 4 shows the microstructures of as-cast composites fabricated under different processing conditions along with corresponding energy-dispersive spectroscopy (EDS) data. Irrespective of the processing condition, all the EDS spectra show a significant presence of Si, C, N and O. Notice that nominal oxygen content in the SiCNO ceramic particles of in-situ composites fabricated at 800°C is significantly higher than that of composites processed at 700°C [1]. Such difference in
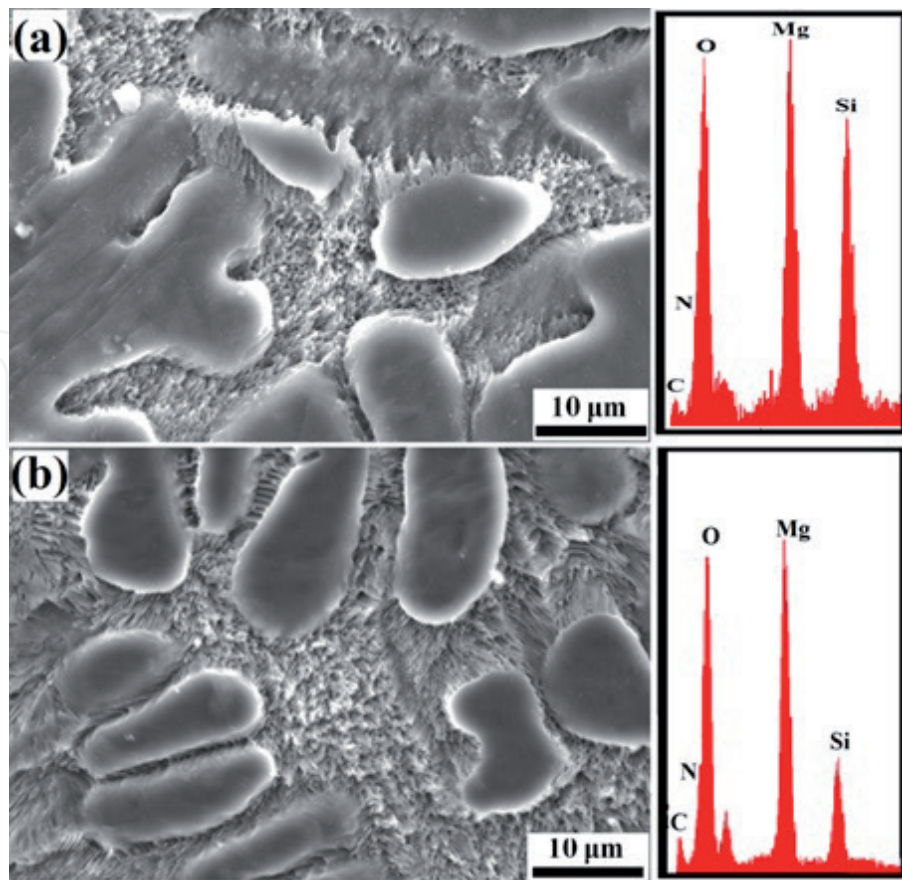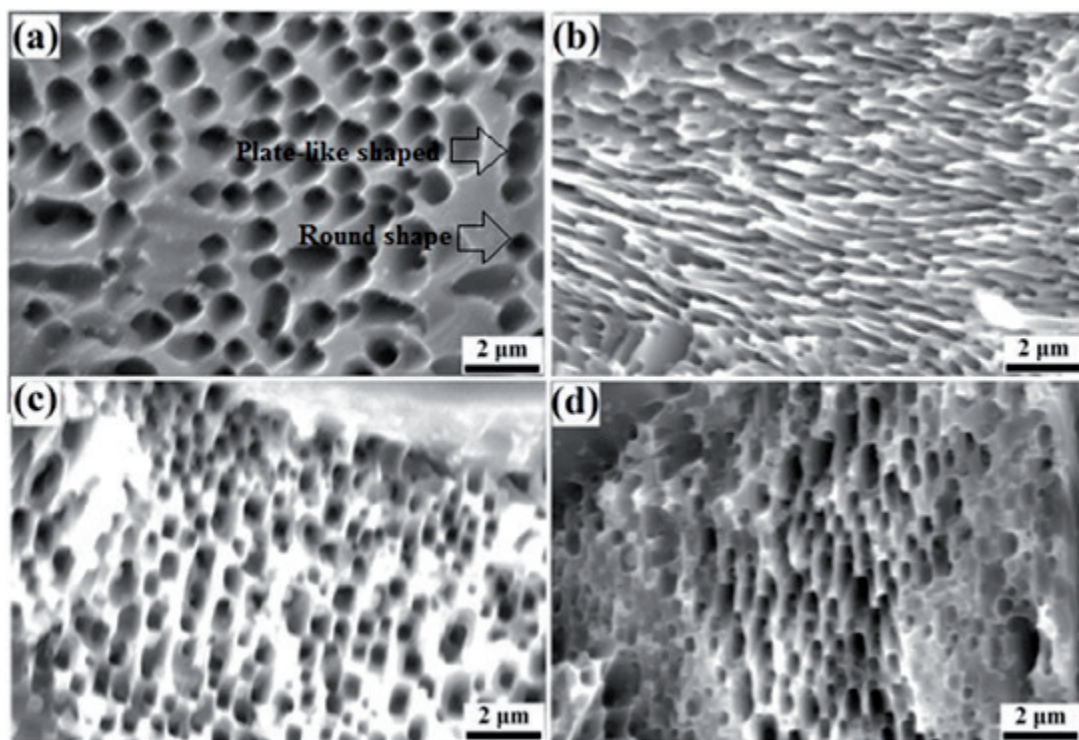

Figure 4.
SEM micrographs of in-situ Mg matrix composites in as-cast condition along with corresponding EDS spectra (a) PP800 composite and (b) PL800 composite [1].

oxygen content arises because of increase in the partial oxidation of organic phase while it was being added into the magnesium melt [25]. Microstructural characterization reveals the fact that the intensity of grain boundary segregation of PDC particles appears to be significantly larger in PP800/PL800 composites as compared to that of PP700/PL700 composites as seen in **Figure 5** [1]. As long as the ceramic particles are being pushed away by the solidification front, the composites having dendritic grain morphology are expected to hold more number of PDC particles at the grain boundaries as compared to the composites with columnar grain morphology during solidification. This can be associated with the fact that each dendritic grain is comprised of six orthogonal primary trunks whereas the columnar grain possesses no such primary trunks [21]. Moreover, the particle sizes of PDC ceramic phase vary with processing temperature. For instance, PP700/PL700 composites are characterized by coarsened round shaped particle having size range of 500 to 700 nm while platelet-like shaped particles have a width of 300 to 400 nm and a length of 2 to 4 μm. However, PP800/PL800 composites depicts slightly fine-sized round shaped particle (having a mean size of about 400 to 500 nm) and platelet-like shaped particles have a width of 100 to 200 nm and a length of 1 to 2 μm. The difference in particle sizes of the fabricated composites could be associated with variation in the intensity of fragmentation of PDC particles during in-situ pyrolysis under different processing temperatures [1].

3.2 Mechanical properties

Figure 6 shows the Vickers hardness data of as-cast in-situ Mg-based P-MMCs along with commercial pure Mg. It was found that the value of hardness of as-cast P-MMCs is enhanced by about 40–75% as compared to that of the base metal. Such enhancement is caused by the reinforcement of PDC particles, and grain size reduction of the as-cast composites. Notice that all hardness measurements are performed in the grain matrix or matrix rich regime of the composites, away from

Figure 5.
Particle morphologies of in-situ Mg matrix composites in as-cast condition (a) PP700 composite (b) PP800 composite (c) PL700 composite and (d) PL800 composite [1].
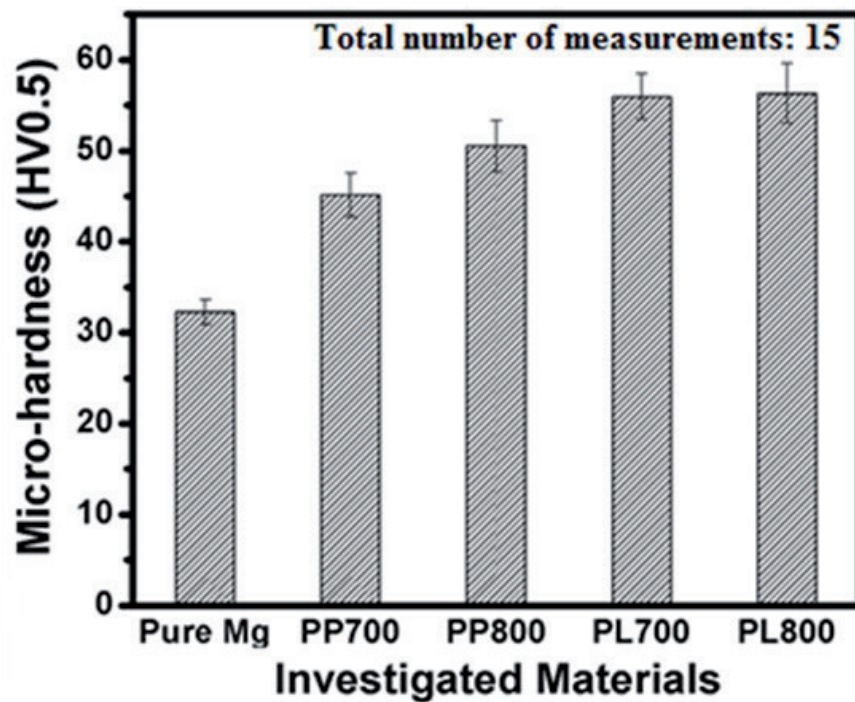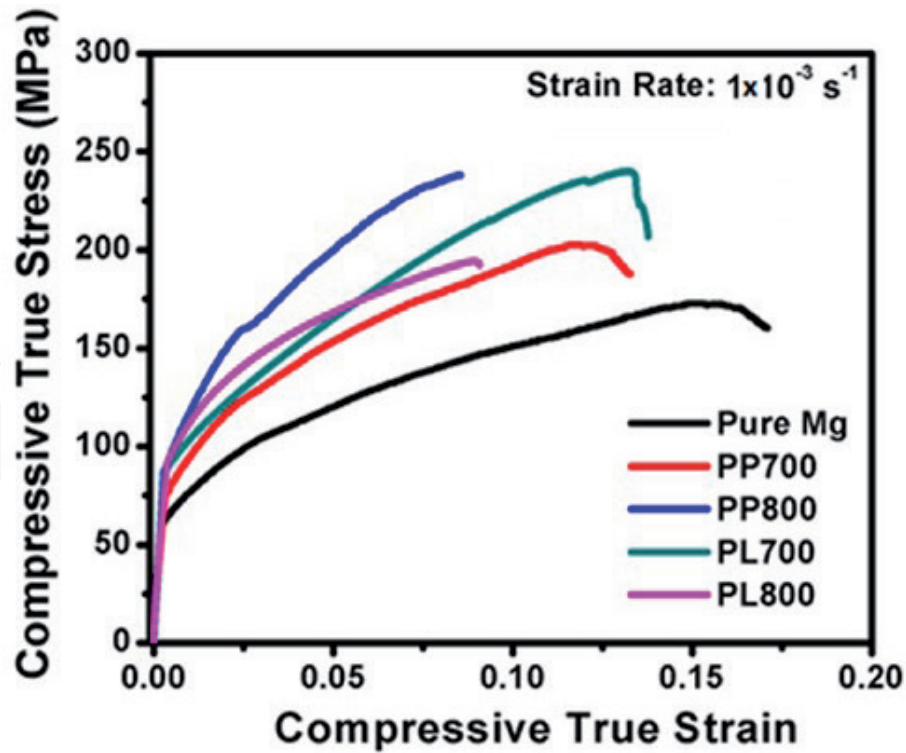
Figure 6.
Micro-hardness properties of pure Mg and in-situ Mg matrix composites [1].

the particles at the grain boundaries but taking care to avoid indentation near the micro-pore area in the as-cast composites in a way to minimize the influence of porosity on the hardness of composites [1]. The hardness data reveals considerable scatter in the values of micro-hardness varying from 45 ± 2 to 56 ± 2 HV. Such a variation arises because of the differences in grain size, volume fraction of in-situ formed PDC particles, and the intensity of grain boundary segregation and formation of Mg_2Si phases in the composites fabricated under different processing conditions [1]. Furthermore, the presence of Mg_2Si crystals in composites fabricated at 800°C exhibits high hardness as compared to that of the composites fabricated at 700°C. This can be attributed to Taylor strengthening mechanism due to thermal mismatch between the matrix and in-situ formed Mg_2Si particles leading to produce significant amount of dislocations at the particle/matrix interface [1].

Figure 7 shows the typical compression true stress-true strain curves of the as-cast composites fabricated under different processing conditions. As depicted in Figure 7, the values of compressive yield stress (CYS) and ultimate compression stress (UCS) of all the as-cast composites are significantly higher when compared to pure magnesium [1]. For instance, it can be noticed that the yield stress for the PP800/PL800 specimen is in the range of 77–90 MPa, whereas 85–88 MPa for the PP800/PP700 specimen, but it is only 60 MPa for pure Mg. Moreover, the values of UCS of PL700/PP800 specimen is in the range of 235–237 MPa, enhanced by 10% and 82% as compared to that of PL800 specimen and pure Mg, respectively [1]. Further, the value of strain to failure of PP800/PL800 specimen experiences the lowest strain to failure (9–10%) when compared to that of PL700 specimen (16–18%) and pure Mg (20–22%). The lowest ductility can be closely associated with the presence of brittle Mg_2Si ceramic phase which often impairs the room temperature plasticity of the composites fabricated at 800°C [1].

Figure 8 illustrates the morphology of the fractured surface for the as-cast PL700 and PL800 composites after compression. As shown in Figure 8, while the fracture surface of PL700 composite shows the mixed mode of failure including both ductile and cleavage patterns, PL800 composite exhibits cleavage mode

Figure 7.
Compression behavior of pure Mg and in-situ Mg matrix composites at room temperature [1].
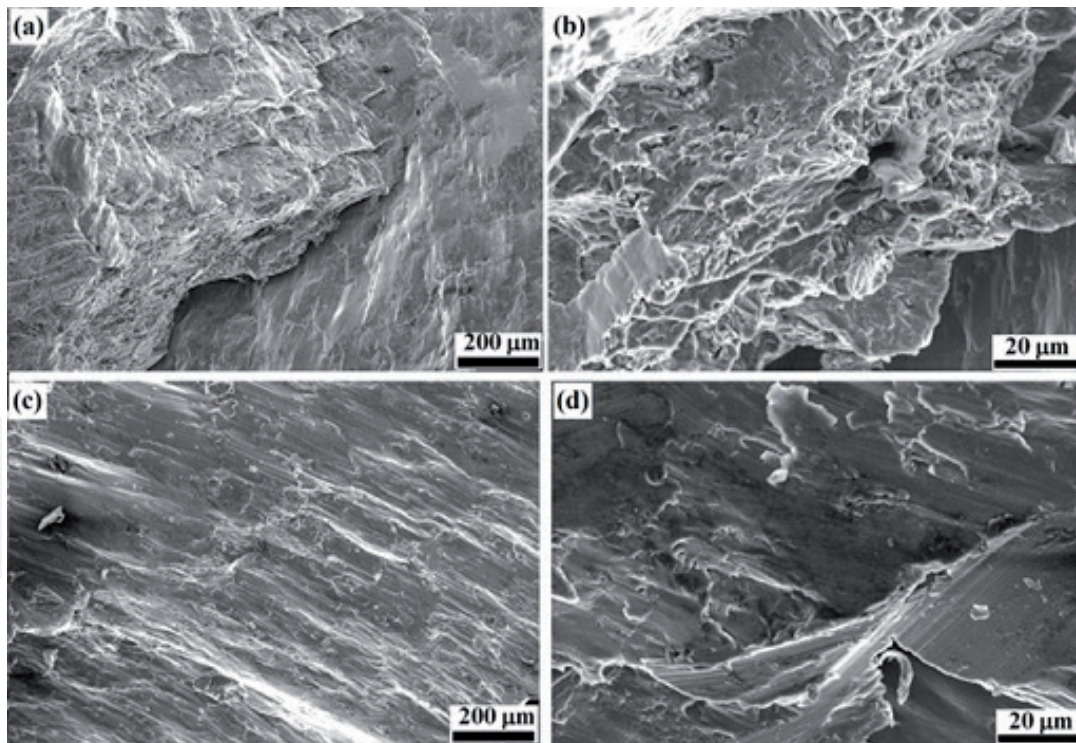
Figure 8.
SEM micrographs of the fracture surface of as-cast Mg matrix composites tested at room temperature (a) and (b): PL700 composite and (c) and (d): PL800 composite [1].

representing brittle fracture. It can be understood clearly that the mechanical properties (CYS, UCS and ductility) of as-cast composites can be improved significantly if one could avoid the formation of brittle Mg$_2$Si ceramic phase in the molten magnesium. This can be achieved by lowing the process temperature from 800 to 700°C during in-situ pyrolysis. Such improvement in mechanical properties of the final composites arises because of two primary reasons namely (i) minimal amount

of grain boundary segregation of PDC particles tending to provide reasonable strengthening of the magnesium matrix, and (ii) reduction in the amount of Mg_2Si crystal within the magnesium matrix leads to cause significant plastic deformation of the composites [1].

4. Structure-property correlation of as-cast In-situ Mg-alloy based metal matrix composites

4.1 Microstructural characteristics

Figure 8 shows the microstructural evolution of as-cast PP900-AZ specimen. It can be evident that the intermetallics of β-$Mg_{12}Al_{17}$ phase are segregated at the grain boundaries as seen in **Figure 9(a)**. Most interestingly, majority of the SiCNO particles (black color) are entrapped within discontinuous network of β-$Mg_{17}Al_{12}$ phase at the vicinity of grain boundaries of PP900-AZ specimen as shown in **Figure 9(b)**. **Figure 9(d)** represents EDS spectra showing the presence of Si, C, and O atoms along with Mg and Al peaks. Microstructural analysis reveals no signature of Mg_2Si particles in the PP900-AZ specimen fabricated at 900°C. This is because of the fact that the existence of large cluster of Al-atoms (of about 9 wt%) in the molten slurry leads to maximize the probability of interrupting the diffusion path for Si-atoms to form any Mg_2Si crystals on heterogeneous substrates of SiCNO particles. This explanation is justifiable due to slower inter-diffusion rate of Al-atoms in the Mg solution as reported by Brennan et al. [1, 26]. However, Sachin et al. [27] observed the formation of in-situ Mg_2Si ceramic phase in the ultrasonic agitated molten AZ91 Mg-alloy after the addition of Si particles. It should be kept in mind that the polymer precursor approach does not involve any ultrasonic assisted vibration treatment of the molten Mg-alloy [1]. Yang et al. [28] mentioned that an ultrasonic vibration
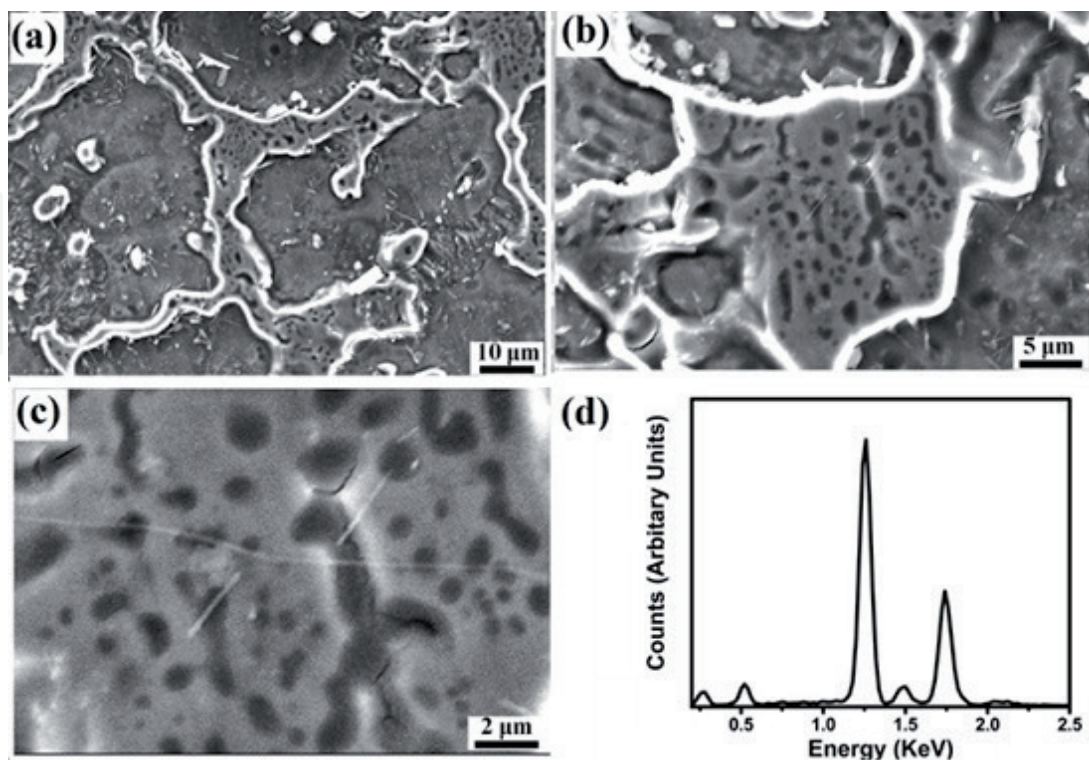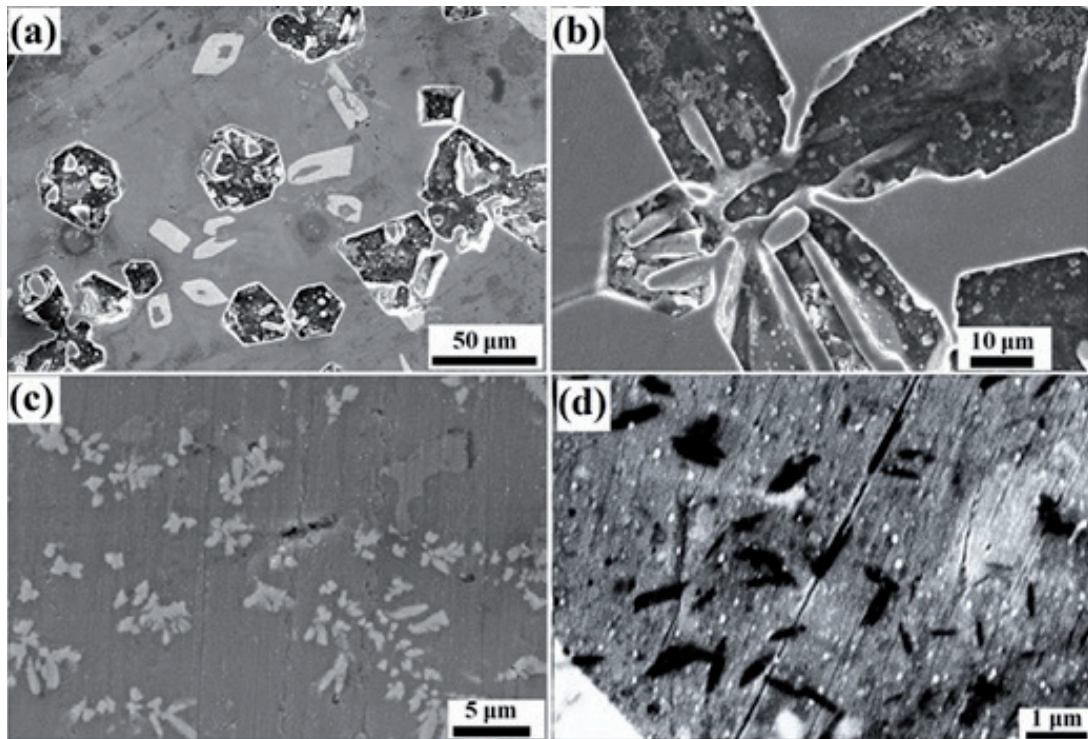

Figure 9.
Microstructural evolution of AZ91 matrix composites (a) β-$Mg_{12}Al_{17}$ intermetallics at the grain boundaries (b) and (c) encapsulation of SiCNO particles within the β-$Mg_{12}Al_{17}$ phase, and (d) EDS spectrum of polymer derived ceramic (SiCNO) particles [1].

can produce transient micro "hot spots" that can take temperature of about 5000°C and pressure above 1000 atmospheres in the melt [1]. Such a drastic variation in temperature–pressure accelerates the reaction kinetics of Mg_2Si formation as explained by Sachin et al. [27]. In addition, Sachin et al. [27] introduced the native powder of Si particles into the Mg-alloy melt which results in intimate physical contact between Si particles and the Mg melt. However, Si-atoms are introduced in the form of cross-linked polymer in the polymer precursor approach [1].

During solidification, molten Mg-alloy can be first transformed into primary α-Mg and β-$Mg_{17}Al_{12}$ phases in accordance with phase diagram. The primary α-Mg phase has limited amount of solubility with Al-atoms depending up on the temperature (maximum solubility of 11.8 at% Al-atoms at 437°C to 1 at% at room temperature). Therefore, Al-atoms have a greater tendency to push away any SiCNO particles to the grain boundaries which eventually leading to particle entrapment by β-$Mg_{12}Al_{17}$ phase. Hashim et al. [29] pointed out that grain boundary segregation of SiC particles occurs in Al-based MMCs owing to poor wettability between Al melt and SiC particles. Despite the fact that SiC and SiCNO particles are chemically distinct, it is justifiable to consider both of them as equivalent in terms of wettability properties with Al-atoms. The formation of Mg_2Si crystals was suppressed as most of the SiCNO particles are entrapped by β-$Mg_{17}Al_{12}$ phase. Under this situation, diffusion of Si-atoms from SiCNO ceramic phase could not take place across the domains of supersaturated α-Mg and β-$Mg_{17}Al_{12}$ phases during solidification. Therefore, the probability of forming Mg_2Si crystal within PP900-AZ composite can be ruled out completely [1].

Figure 10 represents the microstructural characteristics of as-cast PP900-AE specimen. As shown in **Figure 10**, it can be observed that Mg_2Si crystals exhibit dendritic morphology (average particle size of 50–100 μm) along with dispersion of Al_xRE_y intermetallics (acicular shaped gray color particles) in the matrix. The particle size of the fewer Al_xRE_y precipitates are appeared to much finer in size

Figure 10.
Microstructural evolution of AE44 matrix composites (a) dispersion of coarsened Mg_2Si crystals and Al_xRE_y intermetallics (b) dendritic morphology of Mg_2Si crystal (c) dispersion of fine-sized Al_xRE_y intermetallics and (d) uniform dispersion of fine-sized SiCNO particles [1].

as indicated in **Figure 10(c)**. It can be seen 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. (**Figure 10(d)**. During in-situ pyrolysis, the chance of forming Mg_2Si crystals seems to be limited again for the same reasons mentioned earlier for PP900-AZ composite [1]. However, the surrounding medium for nucleating Mg_2Si crystals is completely different during solidification [1]. In AE Series Mg-alloy, the liquid phase was converted in to primary α-Mg phase and Al_xRE_y phase. Most of the Al-atoms are expected to chemically bond with RE elements in the molten Mg-alloys to form an acicular Al_xRE_y precipitates. Moreover, Chen et al. [30] found that addition of RE elements have positive effects on the nucleation of Mg_2Si crystals for the case of Al-Mg-Si alloys. Therefore, the most preferential sites for nucleating Mg_2Si crystals could be the Al_xRE_y precipitates in AE-44 Mg-alloy [1]. Once Mg_2Si crystal is nucleated, and it persists its growth along the preferential growth direction **<100>** to form an equilibrium crystal shape of octahedron morphology. However, the morphology of Mg_2Si crystal changes from octahedral to dendritic shaped crystal because of SiCNO particles in the surrounding medium (**Figure 10(b)**) which may impose space constraint for this equilibrium growth direction (**Figure 10(c)**).

4.2 Mechanical properties

As seen in **Table 2**, the micro-hardness and yield strength data of the fabricated composites reveals that PP900-AE composite experiences hardness or strength enhancement with an increment of 332.0% as compared to that of the base AE44 Mg-alloy. However, there is only marginal increment in the hardness or yield strength 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-$Mg_{17}Al_{12}$ phase (**Figure 8(b)**) [1]. Nevertheless, PP900-AZ composite is expected to offer high temperature creep resistance as unstable β-$Mg_{17}Al_{12}$ phase is dispersed with thermally stable SiCNO particles. The observed significant improvement in hardness for PP900-AE composites is mainly associated with the contribution of Taylor strengthening and load transfer mechanisms. The contribution of Taylor strengthening is massive in case of PP900-AE specimen as compared to that of PP900-AZ specimen. Notice that all of the fabricated in-situ P-MMCs were subjected to temperature difference (ΔT) of about 873 K during solidification processing. Therefore, the probability of achieving highest density of dislocations increases steadily with fabricated composites owing to larger thermal strain induced during solidification. However, thermal mismatch effect loses its importance in first place for the case of PP900-AZ specimen. This can be associated with the entrapment of SiCNO particles by β-Mg17Al12 phase, which in turn generates lesser number of dislocations within the primary α-Mg

	AZ91	AE44	PP900-AZ	PP900-AE
Vicker's hardness, HV	82	58	95	254
Yield strength, MPa	288	206	310	880
Volume fraction of SiCNO		0.0	0.05	0.10
Volume fraction of Mg_2Si		0.0	0.0	0.18

Table 2.
Mechanical properties of the fabricated In-situ Mg-alloy based composites.

phase which eventually leads to a lowest Taylor strengthening. Next to Taylor strengthening, the load transfer strengthening also plays a major role in enhancing the hardness of the fabricated composites. This can be mainly associated with load bearing capacity of hard ceramic phase due to presence of higher volume fraction of reinforced PDC particles (i.e. $V_f \approx 0.28$) in PP900-AE specimen [1].

5. Conclusions

Commercial purity magnesium and Mg-alloys (AZ91 & AE44 series) based composites were fabricated successfully by injecting liquid polymer and cross-linked polymer directly into molten metal/alloys by using liquid stir-casting method via polymer precursor approach. During in-situ pyrolysis, the intensity for formation of brittle Mg_2Si ceramic phase can be minimized by reducing the processing temperature from 800 to 700°C. Most of the polymer derived SiCNO particles are segregated at the grain boundaries because of particle pushing effect by solidification front during solidification. In-situ Mg_2Si crystals were not formed in AZ91 matrix composite because of higher concentration and slower inter-diffusion rate of Al-atoms within molten slurry. To summarize, it may be emphasized that in-situ pyrolysis approach opens an opportunity window for the material researchers to develop futuristic Mg-based hybrid in-situ MMCs owing to the formation of both the 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 applications. Notice that ductility of the composites can be enhanced by controlling the volume fraction, size and morphologies of Mg_2Si crystals in the final composites. This can be achieved via optimization of in-situ processing variables such as pyrolysis or process temperature, pyrolysis time, and cooling rate of casting process.

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References

[1] Nagaraj C.M, Processing and characterization of in-situ magnesium metal matrix composites containing SiCNO particles, [Ph.D Thesis]. Ropar : Indian Institute of Technology; 2017.

[2] Koczak M.J, and Kumar K.S, In-situ process for producing a composite containing refractory material. US Patent 4,808,372, (1989).

[3] Koczak M.J, and. Premkumar M.K, Emerging technologies for the in-situ production of MMCs. JOM-J. Min. Met. Mater. Soc., 1993 : 45 :44-48.

[4] Gibbons T.B, and O'hara S, The effect of internal oxidation on the damping capacity of copper-silicon alloys. J. Phil. Magaz., 1960 :5 : 140-145.

[5] Tjong S.C., and Ma Z.Y, Microstructural and mechanical characteristics of in-situ metal matrix composites, Mater. Sci. Eng. R., 2000 : 29 : 49-113.

[6] Daniel B.S.S, Murthy V.S.R, and Murty G.S, Metal-ceramic composites via in-situ methods, J. Mater. Process. Tech.,1997:68:132-155.

[7] Pradeep K Rohatgi, Ajay Kumar P, Nagaraj M Chelliah, Rajan T.P.D, Solidification processing of cast metal matrix composites over the last 50 years and opportunities for the future, Journal of Metals, 2020 :1:1-15.

[8] Chelliah N.M, Padaikathan P., Surappa M.K., Effects of processing conditions on solidification characteristics and mechanical properties of in situ magnesium metal matrix composites derived from polysilazane precursor, Journal of Composite Materials, 2019 :1 :1-15.

[9] Chelliah N.M, Padaikathan P, Surappa M.K, Deformation mechanisms and texture evolution of in- situ magnesium matrix composites containing polymer derived SiCNO dispersoids during hot compression, Material Science and Engineering: A, 2018 :720:49-59.

[10] Chelliah N.M, Sudarshan, Lisa Kraemer, Singh H, Surappa M.K, Rishi Raj, A polymer route to the design of thermally stable metal matrix composites: Materials selection and in-situ processing, Research and Report on Metals, 2017 :1 :3-7.

[11] Chelliah N.M, Sudarshan, Lisa Kraemer, Singh H., Surappa M.K, Rishi Raj, Stress-rupture measurements of cast magnesium strengthened by in-situ production of ceramic particles, Journal of Magnesium and Alloys, 2017 :5 : 225-230.

[12] Chelliah N.M, Singh H, Surappa M.K., Microstructural evolution and strengthening behavior in in- situ magnesium matrix composites fabricated by solidification processing, Material Chemistry and Physics, 2017 :194 :65-76.

[13] Chelliah N.M, Singh H, Raj R, and Surappa M.K, Processing, microstructural evolution and strength properties of in-situ magnesium matrix composites containing nano-sized polymer derived SiCNO particles, Material Science and Engineering A, 2017 :685 :429-438 DOI:10.1016/j. msea.2017.01.001 (I.F: 3.086)

[14] Raj R, Surappa MK, Process for preparation of nano ceramic-metal matrix composites and apparatus thereof US Patent 8,540,797

[15] Sudarshan, Surappa M. K, Ahn D, and Raj R, Nanoceramic-metal matrix composites by in-situ pyrolysis of organic precursors in a liquid melt, Met. Mater. Trans A., 2008 :39:3291-3297.

[16] Sudarshan, Terauds K, Anil Chandra A. R., and Raj R, Polymer-derived in-situ metal matrix composites created by direct injection of liquid polymer into molten magnesium, Met. Mater. Trans. A., 2014) :45 :551-554.

[17] Castellan E, Ischia G, Molinari A, and Raj R, (2013) A novel in-situ method for producing a dispersion of a ceramic phase into copper that remains stable at 0.9 Tm. Mett. Mater. Trans. A., 2013 : 44 :4734-4742.

[18] Castellan E, Kailas S.V, Madayi S, and Raj R, Low-wear high-friction behavior of copper matrix composites dispersed with an in-Situ polymer derived ceramic, J. Tribology.,2015:137:024501.

[19] Kumar A, Raj R, and Kailas S.V, A novel in-situ polymer derived nano ceramic MMC by friction stir processing, Mater. Des., 2015: 85:626-634.

[20] Kroke E, Li Y.L, Konetschny C, Lecomte E, Fasel C, and Riedel R, Silazane derived ceramics and related materials. Mater. Sci. Eng. R, 2000 :26 : 97-199.

[21] Yuan X, Sun W, Du Y, Zhao D.D and H. Yang, Thermodynamic modeling of the Mg–Si system with the Kaptay equation for the excess Gibbs energy of the liquid phase, Calphad., 2009 :33 : 673-678.

[22] Inem B, and Pollard G., Interface structure and fractography of a magnesium-alloy, metal-matrix composite reinforced with SiC particles, J. Mater Science,1993 :28 :4427-4434.

[23] Kurtz W, and Fisher D.J, Fundamentals of solidification, 1st ed, Switzerland, Trans Tech Publication ; 1986.

[24] Kim G.H, Hong S.M, Lee M.K, and Kim I.S, Effect of oxide dispersion on dendritic grain growth characteristics of cast aluminum alloy, Mater. Trans., 2010 : 51:1951-1957.

[25] Sudarshan, Magnesium matrix-nano ceramic composites by in-situ pyrolysis of organic precursors in a liquid melt [Ph.D Thesis]. Bangalore : Indian Institute of Science ; 2010.

[26] Brennan S, Warren A.P, Coffey K.R,. Kulkarni N, Todd P,. Kilmov M, and Sohn Y.H, Aluminum Impurity Diffusion in Magnesium, J. Phase Equil. Diff., 2012 :X :121-125.

[27] Sachin V.M, Singh S.P, Sinha P, Bhingole P, and Chaudhari G.P, Microstructural evolution in ultrasonically processed in situ AZ91 matrix composites and their mechanical and wear behavior, Mater. & Des., 2014 : 53:475-481.

[28] Yang Y, Li X, and Cheng X, Ultrasonic assisted fabrication of metal matrix nanocomposites, J. Mater. Sci., 2004 :39 :3211-3212.

[29] Hashim J, Looney L, and Hashmi M.S.J, The wettability of SiC particles by molten aluminum alloys, J. Mater. Proc. Tech., 2001 :11 :9324-328.

[30] Chen Z, Hao X, Zhao J. and Ma C, Kinetic nucleation of primary a(Al) dendrites in Al-7%Si-Mg with Ce and Sr additions, Trans. Non. Ferr. Met. Soc. China., 2013 :23 :3561-3567.