RECENT DEVELOPMENTS ON ULTRASONIC CAVITATION BASED SOLIDIFICATION PROCESSING OF BULK MAGNESIUM NANOCOMPOSITES

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Abstract

This paper presents the results from our recent development in cast bulk Mg nanocomposites. SiC nanoparticles reinforced magnesium and magnesium alloys including pure magnesium, and Mg-(2, 4)Al-1Si and Mg-4Zn were successfully fabricated by ultrasonic cavitation based dispersion of SiC nanoparticles in magnesium melt. As compared to un-reinforced magnesium alloy matrix, the mechanical properties including tensile strength and yield strength were improved significantly while the ductility was retained or even improved. In the microstructure, the grain size was refined considerably by SiC nanoparticles. While some micro SiC clusters still exist in the magnesium matrix, ultrasonic cavitation based processing is very effective in dispersing SiC nanoparticles. A SEM study showed that SiC nanoparticles were dispersed quite well in the areas outside micro SiC clusters. A TEM study on the interface between SiC nanoparticles and magnesium alloy matrix indicates that SiC nanoparticles bonded well with Mg matrices without forming an intermediate phase.

Keywords: *magnesium, nanocomposites, ultrasonic cavitation and dispersion.*

Introduction

Magnesium based metal matrix composites (MMCs) have been extensively studied as an attractive choice for automotive and aerospace applications due to their low density and superior specific properties including strength, stiffness and creep resistance. Xi *et al* [1] studied the Ti-6Al-4V particulate (TAp) reinforced magnesium matrix composite which is fabricated by powder metallurgy route. The tensile strength of the composite was markedly higher than that of the unreinforced magnesium alloy. Xi *et al* [2] also studied the SiC whiskers-reinforced MB15 magnesium matrix composites by powder metallurgy and found that the mechanical properties of SiCw/MB15 composite were significantly influenced by powder-mixing methods of PM. Li *et al* [3] studied the hot deformation behavior of SiC whiskers reinforced AZ91 magnesium matrix composites in compression. It was found that the microstructure evolutions involved the movement of SiC whiskers and the changes of the matrix, and the rotation and the broken SiC whiskers tended to be obvious with the increasing strain, and also high density of dislocation was observed in the AZ91 matrix at the initial stage of compression (1%). Jiang *et al* [4] studied that magnesium metal matrix composites (MMCs) reinforced with B4C particulates fabricated by powder metallurgy. The hardness and wear resistance of the composites were higher than those of as-cast Mg ingot and increased with increasing amount of B4C particulates from 10 to 20 vol.%. Zhang *et al* [5] studied that carbon nanotube reinforced magnesium metal matrix composite by stirring the carbon nanotube into magnesium melts. It was found that carbon nanotube, especially chemical nickel-plated one, has an excellent role in strengthening the magnesium. The structure of magnesium was refined. The tensile strength and elongation of the composite were also improved. Ma *et al* [6] studied the TiB2-TiC particles reinforced AZ91D alloy. The results showed that the hardness and wear resistance of the composites were higher than those of the unreinforced AZ91 alloy. Pahutova *et al* [7] studied the creep resistance of squeeze cast AZ91 and QE22 magnesium alloys reinforced by 20 vol% Al2O3 short fibers and showed that the creep resistance of reinforced materials was considerably improved compared to the monolithic alloys. Ye *et al* [8] reviewed the recent progress in magnesium matrix composites. The conventional methods such as stir casting, squeeze casting, and powder metallurgy were mostly used in fabricating the magnesium matrix composites reinforced by powders/fibers/whiskers. Some other processing techniques such as *in-situ* synthesis, mechanical alloying, pressureless infiltration, gas injection, and spray forming were also sometimes used. For magnesium matrix composites, the mechanical properties such as tensile strength, creep resistance and fatigue resistance were improved, but at the cost of other properties, typically ductility. The poor ductility of magnesium matrix composites limits the widespread application of Mg based MMCs.

Nanoparticle reinforcements can significantly increase the mechanical strength of the matrix by more effectively promoting particle hardening mechanisms than micron size particles. A fine and uniform dispersion of nanoparticles provides a good balance between the strengthener (non-deforming particles, such as SiC nanoparticles) and inter-particle spacing effects to maximize the yield strength and creep resistance. It is expected that the properties of metals reinforced by ceramic nanoparticles (less than 100 nm), that is, metal matrix nanocomposites (MMNCs), would be enhanced considerably (e.g. superior strength and creep property at elevated temperatures, higher fatigue life, and better machinability) while the ductility of the magnesium matrix is retained.

Solidification processing such as stir casting that utilized mechanical stirring was a widely used technique to produce magnesium matrix composites that were reinforced by micro ceramic particles. A combination of good distribution and dispersion of micro particles can be achieved by mechanical stirring. However, to produce magnesium matrix nanocomposites, it is extremely challenging for the conventional mechanical stirring method to distribute and disperse nanoparticles uniformly in metal melts because of the much higher specific surface areas in nanoparticles. In order to achieve a uniform dispersion and distribution of nanoparticles in magnesium matrix nanocomposites, Lan *et al* [9], Li *et al* [10], and Yang *et al* [11] developed a new technique that combined solidification processes with ultrasonic cavitation based dispersion of nanoparticles in metal melts. It was reported [13] that ultrasonic cavitation can produce transient (in the order of nanoseconds) micro "hot spots" that can have temperatures of about 5000°C (9032 °F), pressures above 1000 atms, and heating and cooling rates above 10^{10} °K/s . The strong impact coupling with local high temperatures can potentially break nanoparticle clusters and clean the particle surface. Since nanoparticle clusters are loosely packed together, air could be trapped inside the voids in the clusters, which will serve as nuclei for cavitations. The size of the clusters ranges from nano- to micro-meters due to the attraction force among nanoparticles and the poor wettability between nanoparticles and metal melts.

In this paper, SiC nanoparticles reinforced pure magnesium, Mg-4Zn and Mg-(2, 4)Al-1Si were fabricated by ultrasonic cavitation based solidification processing. The microstructure and overall mechanical properties of nanocomposites were studied to understand the effect of nanoparticles in as cast Mg alloys.

Experimental

Figure 1 shows the schematic experimental setup for the ultrasonic cavitation based fabrication of nano-sized SiC reinforced magnesium matrix nanocomposites. It mainly consists of a resistance heating furnace for melting magnesium, nanoparticle feeding mechanism, protection gas system, and ultrasonic processing system. A mild steel crucible, which is 114 mm in inside diameter (ID) and 127 mm in height, was used for melting and ultrasonic processing. A Permendur power ultrasonic probe, made of C-103 niobium alloy was used to generate a 17.5KHz and maximum 4.0 kW power output for melt processing. The niobium probe is 35 mm in diameter and 39 cm in length. The ultrasonic probe was dipped into the melt for about 32 mm. The melt temperature for ultrasonic processing was controlled at about 700°C (1292°F). Nb is a high temperature element and does not react with Mg at the melt temperature. Nano-sized β-SiC particles were fed into the Mg melt through a steel tube. The average size of the SiC particles used in this study was about 50 nm.

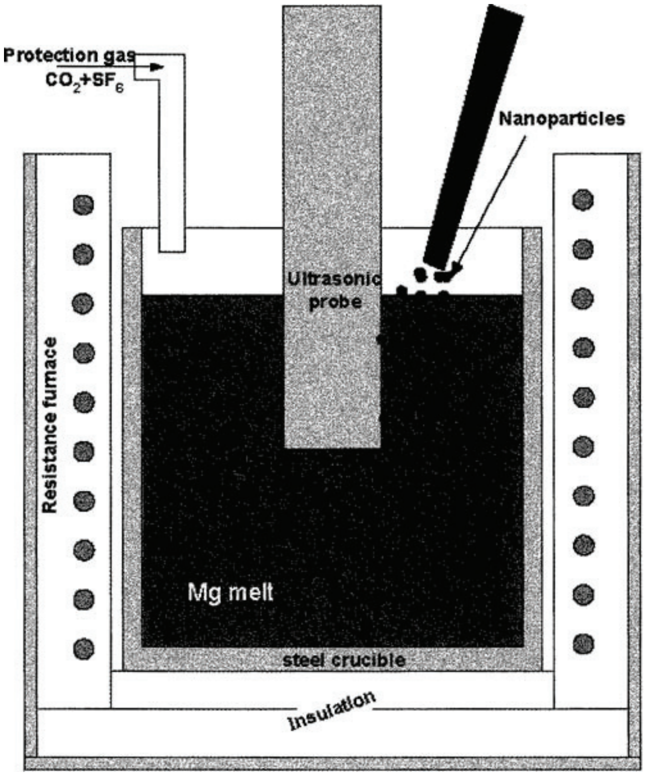


Figure 1. Experimental set-up for fabricating Mg-SiC nanocomposites.

About 800 to 900g of pure (99.8%) magnesium or magnesium alloys were used. The magnesium melt pool was protected by CO_2+ 0.75% SF_6. Pure Mg and pure (99.99%) Zn were used for making Mg-4Zn alloy matrix. After pure Mg was melted, pure Zn was added into the Mg melt. Pure Mg, pure Al and Al-50%Si master alloy were used for making Mg-2Al-1Si and Mg-4Al-1Si matrices. Similar to melting of Mg-4Zn matrix alloy, pure Al and Al-50%Si master alloy were added into the magnesium melt after Mg was melted. It should be noted that no Zr element was added. Zr is an effective grain refiner in Mg alloys that contain no Al or Mn. It is expected that SiC nanoparticles can refine the grain size of Mg alloys significantly. After ultrasonic processing, the magnesium melt was cast into a steel permanent mold that was preheated to about 400°C (752 °F). The mold was designed and fabricated according to ASTM B 108-03a. In each casting experiment, two standard tensile specimens as shown in Fig.2 can be obtained. An additional graphite pouring cup was used to guide the melt and serve as housing for the SiC ceramic filter, which has a dimension of 55 mm x 55 mm x 12 mm and an average pore size of 2.3 mm to 2.9 mm.

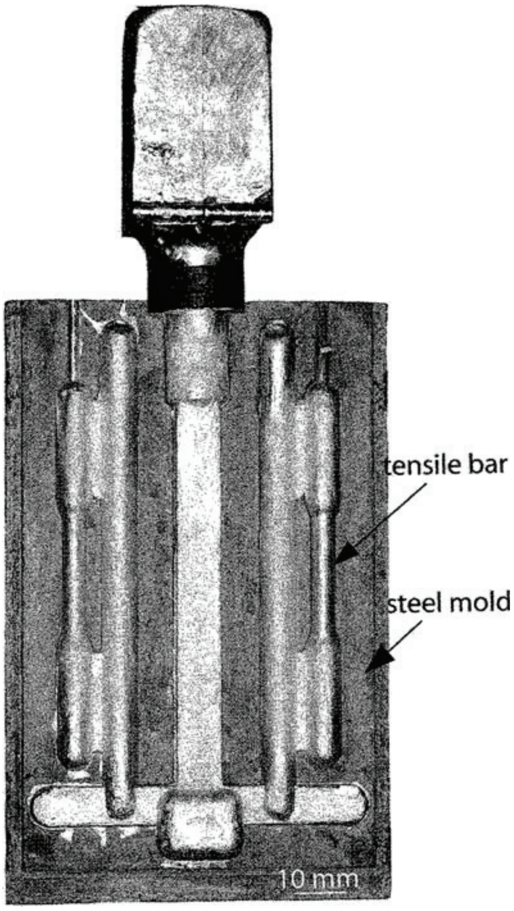


Figure 2. Permanent mold casting samples for tensile testing.

To obtain mechanical properties, specimens with a diameter of 0.375" (9.5 mm) and a gage length of 1.75" (44.5 mm) were tested in a MTS tensile testing machine. In order to get the precise value of yield strength, an extensometer with a 1" (25.4 mm) gage length was clamped to each tensile sample. The cross head speed is set to be 5 mm/min. When the strain reaches 1%, the tensile testing machine will pause temporally so that the extensometer can be taken off. At the first stage of tensile testing, the strain data comes from the extensometer. After the extensometer is taken off, the tensile testing continues and the strain data comes only from the displacement reading of the tensile testing machine.

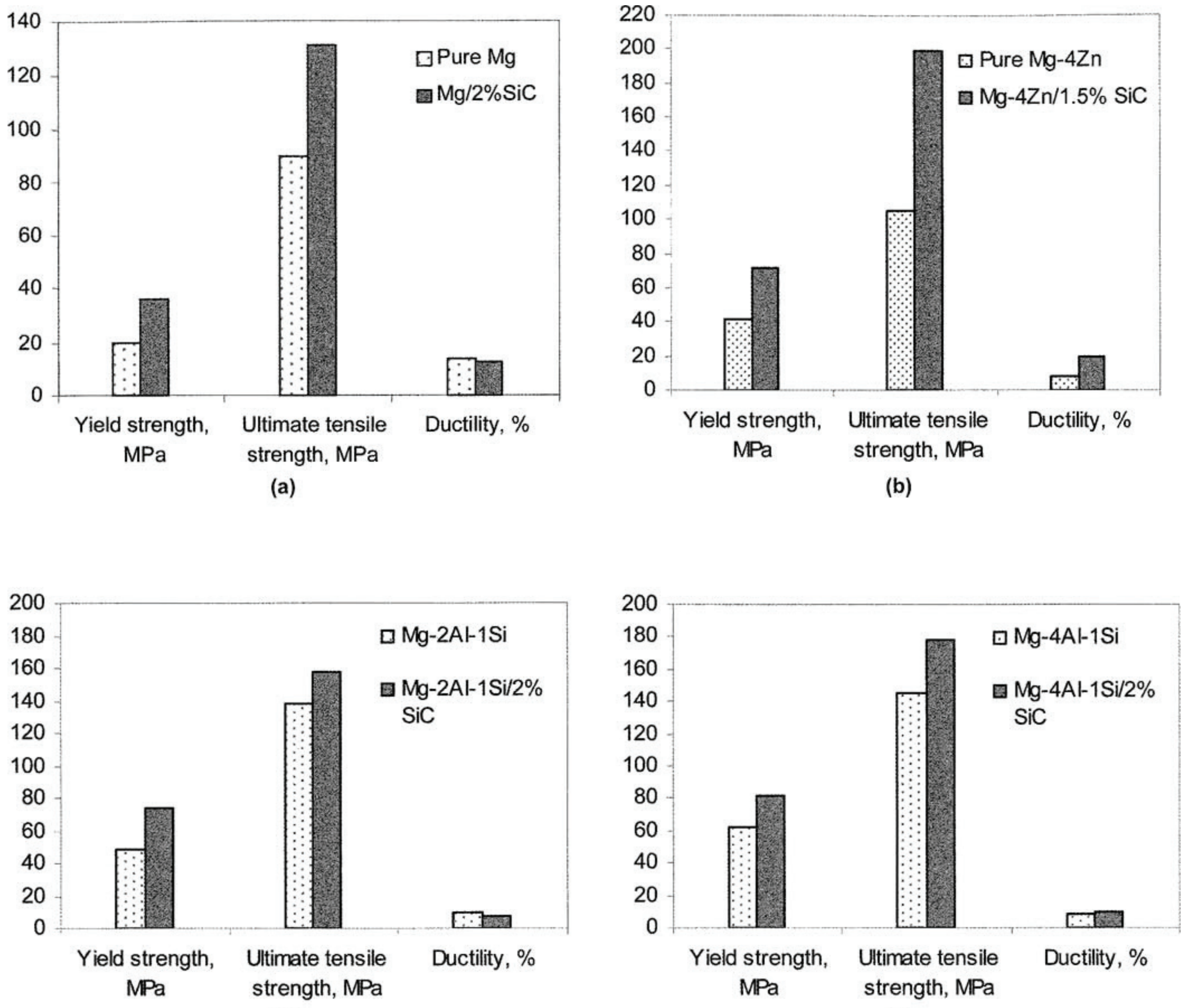
The microstructure of the samples was studied by optical microscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The magnesium nanocomposites samples for optical microscopy and SEM were cut, mounted, mechanically ground and polished. TEM samples were prepared using ion milling.

Results and Discussion

Figure 3a through 3d show the strengthening effects of SiC nanoparticles on the mechanical properties of pure magnesium, Mg-4Zn and Mg-(2, 4)Al-1Si. The yield strength of Mg/2%SiC increased 80%, as compared to that of pure Mg. The good ductility of pure magnesium is also retained in Mg/2%SiC. The mechanical properties of nanocomposites are very different from those of composites materials reinforced by micropowders, in which ductility decreased while the yield strength and ultimate tensile strength were improved [9]. . In Mg-4Zn/1.5%SiC, the yield strength and ultimate tensile strength increased 73% and 90% respectively, and the ductility was also improved significantly. In pure Mg-4Zn, the ductility was about 9%, but in Mg-4Zn/1.5%SiC, the ductility reached over 20%, which was more than twice that of pure Mg-4Zn alloy matrix. This possibly could be attributed to, at least, to the following three aspects: Firstly, although these SiC clusters appeared as micro clusters, most of the nanoparticles in the micro-clusters are still separated to single nanoparticles or sintered nano-clusters. Secondly, the negative effects of some SiC micro-clusters were balanced by the positive effects of the grain refining effects and strengthening effects of the well dispersed SiC nanoparticles. Thirdly, the improvement of ductility in Mg-4Zn/1.5%SiC nanocomposites can also be partly attributed to the decreasing of porosity and crack-like shrinkage areas in Mg-4Zn. Because of the wide freezing temperature range of Mg-4Zn, some porosity and crack-like shrinkage areas formed at the end of solidification. These porosity and crack-like shrinkage areas are detrimental to the ductility. However, this is the first time in our study to show this significant ductility-enhancing effect for as-cast Mg matrix nanocomposites. Normally, the ductility of as cast magnesium nanocomposites (e.g. pure Mg reinforced by SiC nanoparticles) was only retained. While the mechanism for this significant ductility enhancement is not well understood, it certainly warrants further study.

In Mg-2Al-1Si/2%SiC and Mg-4Al-1Si/2%SiC nanocomposites, the yield strength and ultimate tensile strength increased significantly while the good ductility of Mg-2Al-1Si and Mg-4Al-1Si was also retained. From the tensile testing of Mg/2%SiC, Mg-4Zn/1.5%SiC and Mg-(2, 4)Al-1Si/2%SiC, the yield strength and ultimate tensile strength of all three nanocomposites materials were improved significantly and the good ductility of the unreinforced matrix was retained or even improved. The combination of higher strength and good ductility of magnesium matrix nanocomposites is promising for structural applications in various industries.

According to a recent published analytical model [14] for predicting the yield strength of particulate reinforced metal matrix nanocomposites, the strengthening of nanoparticles come from the Orowan strengthening effects, enhanced dislocation density and load bearing effects. It is pointed that Orowan strengthening is not significant in metal matrix composites enhanced by microparticles and it becomes more favorable in metal matrix nanocomposites due to that the Orowan bowing is necessary for dislocations to bypass the nanoparticles. A small volume fraction of nanoparticles can significantly improve the yield strength of metal matrix nanocomposites. This is also a clear contrast to the magnesium matrix composites reinforced by micro particles or fibers, which contains 10 to 30 vol% reinforcement phases.

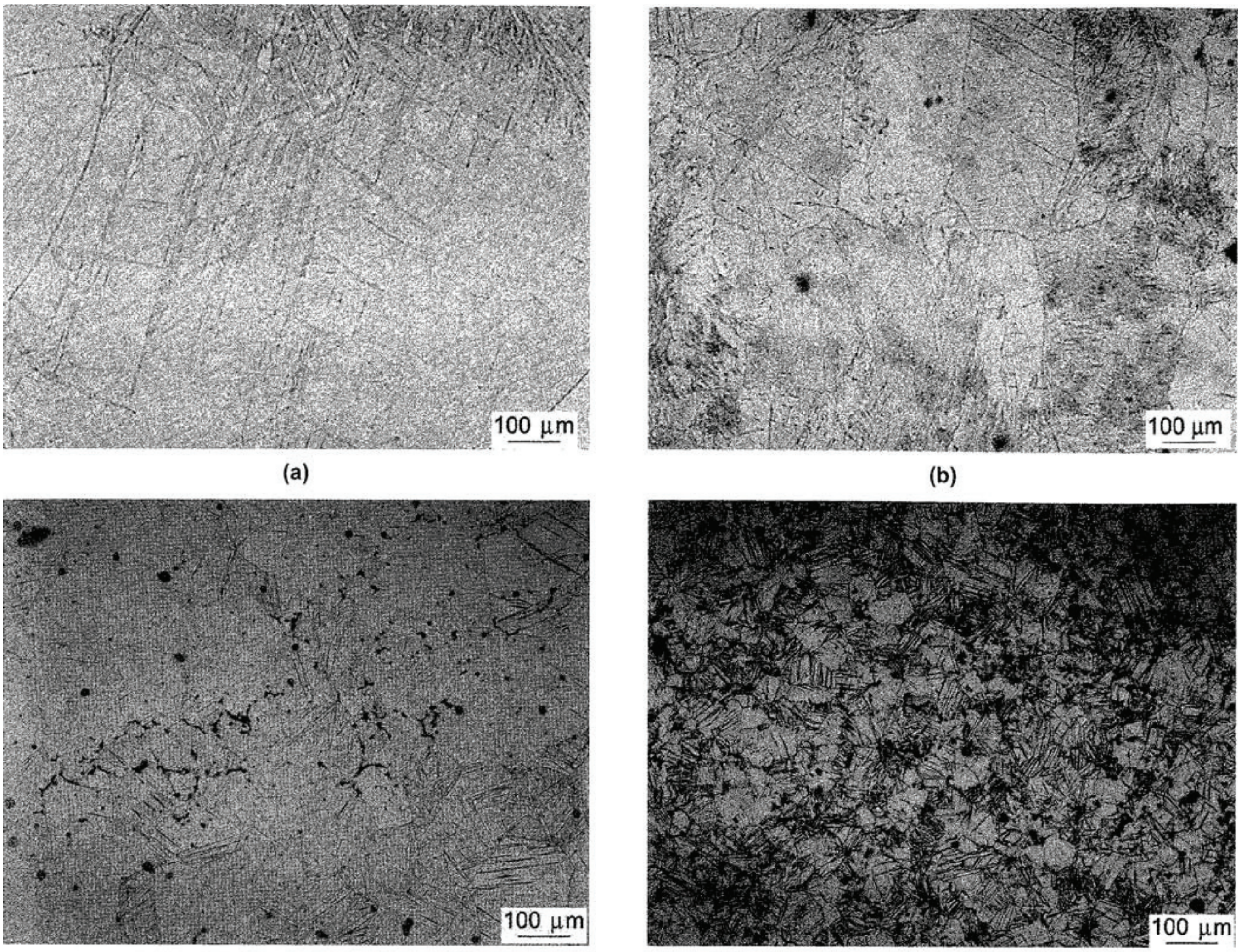


(a) (b)

(c) (d)

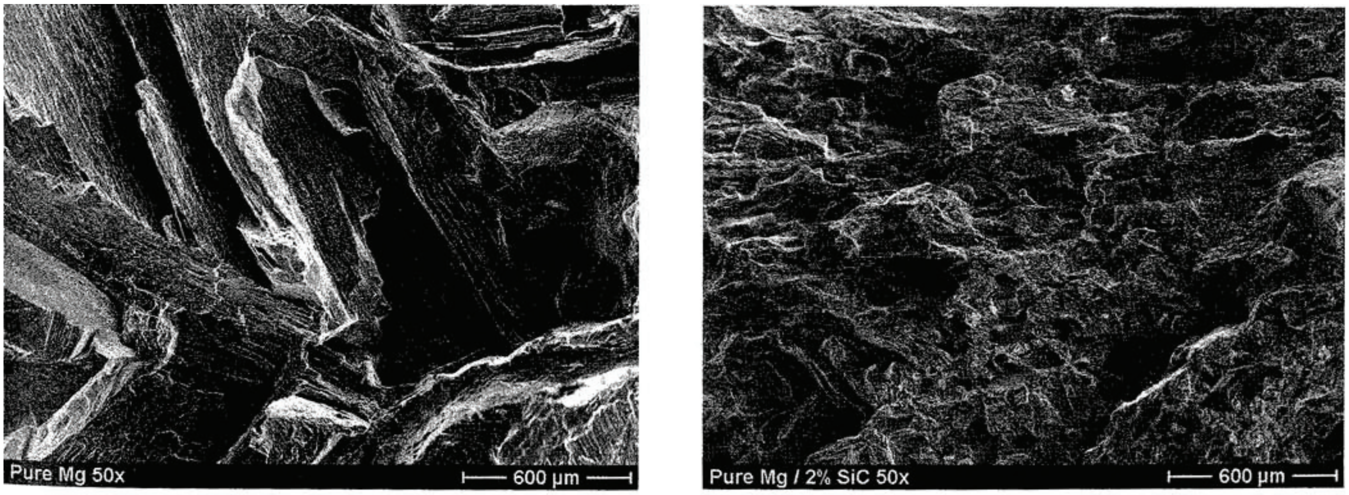
Figure 3. Mechanical properties of (a) pure Mg and Mg/2%SiC, (b) Mg-4Zn and Mg-4Zn/1.5%SiC, (c) Mg-2Al-1Si and Mg-2Al-1Si/2%SiC, (d) Mg-4Al-1Si and Mg-4Al-1Si/2%SiC.

Figure 4 shows the optical microstructures of pure magnesium, Mg/2%SiC, Mg-4Zn, and Mg-4Zn/1.5% SiC. The grain size in Mg/2%SiC is much finer than that in pure Mg, as shown in Fig 4a and b. The grain refinement can also be seen from SEM images (as shown in Figure 5a and b) of the fracture surfaces of pure Mg and Mg/2%SiC samples after they are tensile tested. Similarly, the microstructure of Mg-4Zn/1.5%SiC is also refined by the addition of SiC nanoparticles. In as cast Mg-4Zn, the average grain size is about 150 μm while in as cast Mg-4Zn/1.5% SiC nanocomposits, the average grain size is reduced to about 60 μm. According to the classic Hall-Petch equation: $\sigma_y = \sigma_0 + K_y d^{-1/2}$, where σ_y is the yield strength, σ_0 and K_y are material constants, and d is the mean grain size. The value of K_y is dependent on the number of slip systems. It is higher for HCP metals than for FCC and BCC metals [9]. Since Mg is an HCP metal, the grain size affects the yield strength more significantly. It is also well known that grain size has a strong effect on the ductility and toughness of materials. The significant improvement of yield strength can be attributed to the grain refining effects and strengthening effects of nanoparticles including Orowan strengthening effects, enhanced dislocation density and load bearing effects.



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

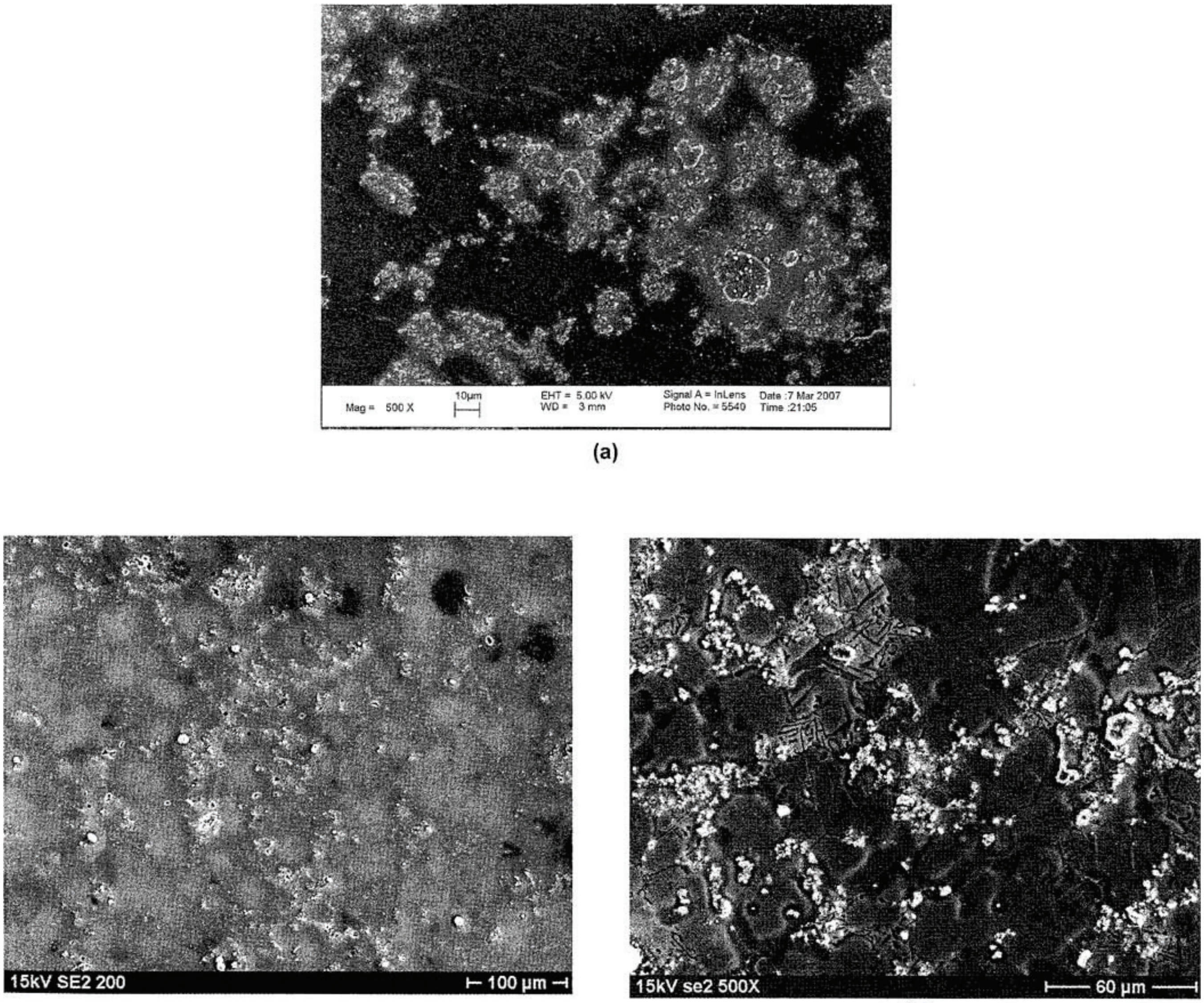
Figure 4. Optical microstructure of (a) pure Mg, (b) Mg/2%SiC, (c) Mg-4Zn and (d) Mg-4Zn/1.5%SiC.



(a) (b)

Figure 5. Fracture surface of (a) pure Mg and (b) Mg/2%SiC.

In the microstructure of Mg-4Zn, as shown in Fig.4c, some shrinkage porosity was observed. This could be due to a very wide solidification range for Mg-4Zn when compared to other magnesium alloys such as AZ91D and Mg-Al alloys. The wide freezing range also results in poor castability. It was also worth mentioning that the castability of Mg-4Zn/1.5% SiC was also improved considerably as compared to pure Mg-4Zn alloy. Little hot tearing existed in as cast Mg-4Zn/1.5% SiC nanocomposites. The fluidity of Mg-4Zn/1.5%SiC nanocomposites melt is also significantly higher than that of Mg-4Zn melt. In casting pure Mg-4Zn alloys, a temporary pause of Mg-4Zn melt can be seen immediately after the melt is poured into the pouring cup, while no temporary pause in the case of Mg-4Zn/1.5%SiC nanocomposites can be noticed. The considerable improvement in castability can be attributed to a finer grain size in Mg-4Zn/1.5% SiC castings and a higher fluidity of Mg-4Zn/1.5%SiC melt. Generally, a finer grain size can improve melt feeding characteristics, increase hot tearing resistance, and minimize shrinkage and porosity.



(a)

(b)

(c)

Figure 6. SEM images of (a) Mg/2%SiC, (b) Mg-2Al-1Si/2%SiC and (c) Mg-4Zn/1.5%SiC.

Figure 6a shows a low magnification SEM image of Mg/2%SiC nanocomposites. The white areas are SiC clusters. These clusters were distributed uniformly. Although ultrasonic cavitation is quite effective in dispersing SiC nanoparticles, the processing parameters were still not optimized. Further improvement on the dispersion of nanoparticles is needed. Similar to Mg/2%SiC nanocomposites, some SiC clusters still existed in the Mg-2Al-1Si/2%SiC and Mg-4Zn/1.5%SiC nanocomposites and they also distributed uniformly as shown in Fig. 6b and 6c.

Figure 7 shows a higher magnification SEM image outside the area of SiC clusters in the Mg/2%SiC sample. It is clear that SiC nanoparticles were dispersed very well. The significant improvement of mechanical properties would mostly be attributed to the well dispersed SiC nanoparticles. In Fig.7, it seems that some of the nanoparticles were even sintered. From the low magnification SEM images, one would expect the ductility of Mg/SiC nanocomposites would be reduced due to the clusters. However, the tensile testing showed that the ductility of Mg/SiC nanocomposites was still high. This possibly can be explained from the following two aspects: Firstly, although these SiC clusters appeared as micro clusters, they are still separated by magnesium between the nanoparticles inside the small clusters and they are different from the SiC micro powders in conventional MMCs. Secondly, the negative effects of SiC clusters were balanced by the positive effects of the grain refining effects and strengthening effects of the well dispersed SiC nanoparticles.

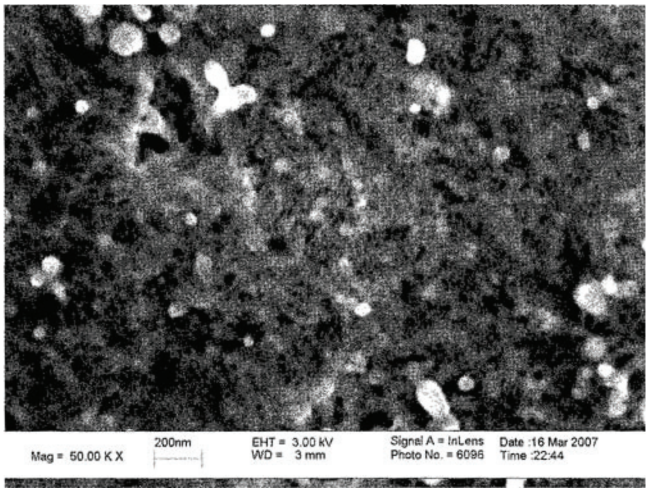
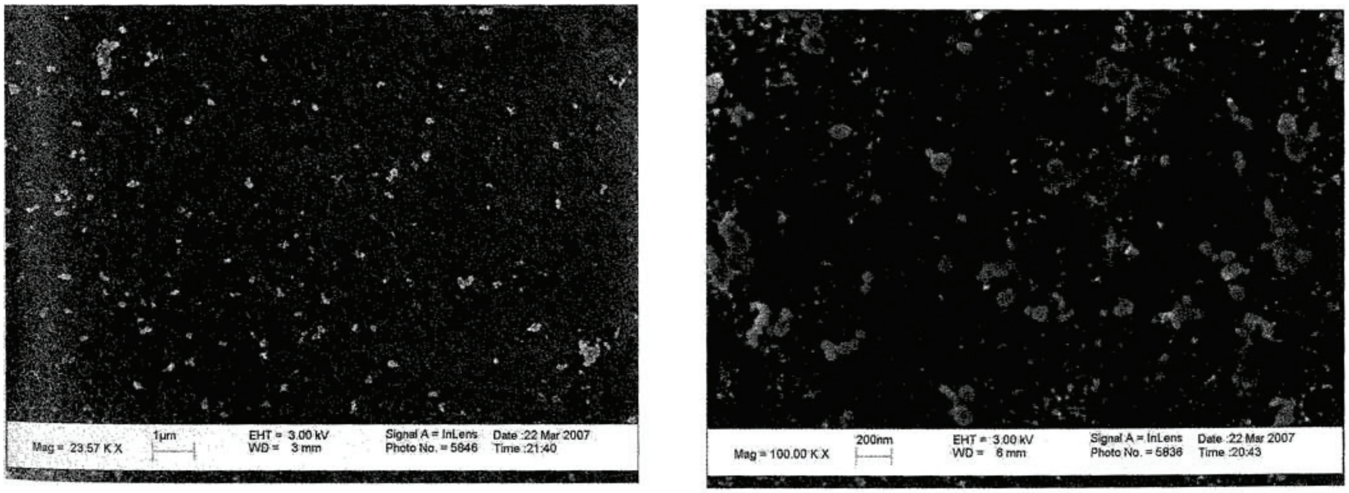


Figure 7. Higher magnification SEM image of Mg/2%SiC.

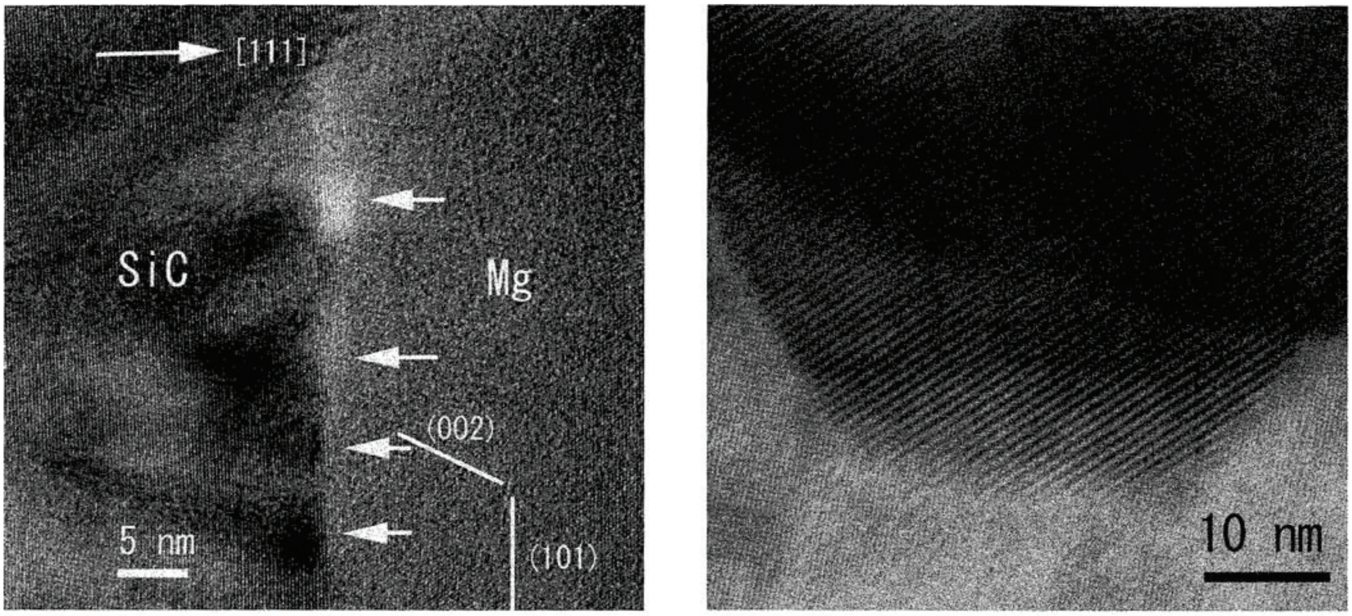


(a) (b)

Figure 8. SEM images of (a) Mg-2Al-1Si/2% SiC nanocomposites and (b) Mg-4Zn/1.5% SiC.

Similarly, from the SEM images of Mg-2Al-1Si/2%SiC and Mg-4Zn/1.5%SiC nanocomposites as shown in Fig. 8a and 8b, SiC nanoparticles were also dispersed quite well. From the above SEM images, it suggests that ultrasonic cavitation processing was very effective in dispersing SiC nanoparticles. This good dispersion was very difficult to obtain via traditional mechanical stirring.

Fig. 9a and 9b show TEM images of the interface between SiC nanoparticles and the magnesium or Mg-4Zn matrix. No intermediate phase occurs, which suggests that there is little reaction between SiC nanoparticle and magnesium or Mg-4Zn matrix. In Fig. 9a, strain contrast was observed near the interface, indicating that SiC are bonded to magnesium very well. Fig. 10 showed the TEM image of the interface between of SiC nanoparticle and Mg-4Al-1Si matrix. It showed a good bonding between SiC and Mg-4Al-1Si matrix, and no intermediate phase was detected.



(a) **(b)**

Fig.9. TEM image of the interface of (a) SiC and Mg in Mg/2%SiC, (b) SiC and Mg-4Zn in Mg-4Zn/1.5%SiC.

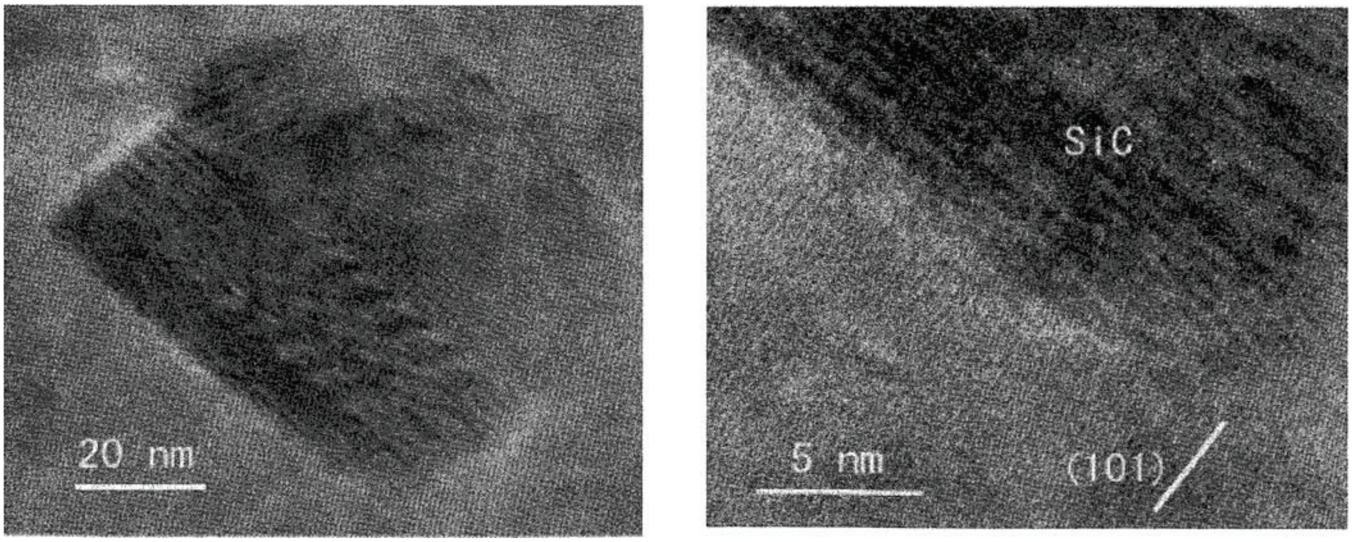


Figure 10. Interface between SiC and Mg-4Al-1Si alloy matrix. SiC grain shows Moire fringes. Mg-4Al-1SiC alloy matrix only shows (101) fringe, suggesting that SiC bond to Mg-4Al-1Si alloy matrix without forming an intermediate phase.

Summary

The yield strength and ultimate tensile strength of Mg/2%SiC, Mg-4Zn/1.5%SiC and Mg-(2, 4)Al-1Si/2%SiC nanocomposites were improved significantly as compared to those of unenhanced pure magnesium, Mg-4Zn and Mg-(2, 4)Al-1Si matrices. The good ductility of the matrices was also retained or even improved. The ductility of Mg-4Zn/1.5% SiC was twice that of pure Mg-4Zn. While the mechanism for this significant ductility enhancement is not understood, it is certainly of interest for future study. SEM study showed that ultrasonic cavitation was an effective way to disperse SiC nanoparticles in magnesium melt. With the addition of SiC nanoparticles, the grain size of magnesium and Mg-4Zn nanocomposites was refined significantly. The castability of Mg-4Zn/1.5% SiC was also improved considerably, as compared to that of pure Mg-4Zn. TEM study indicated that SiC nanoparticles bonded well with the matrices without forming any intermediate phase.

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