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Preparation and characterization of aluminum borate whisker reinforced magnesium alloy composites by semi-solid process

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Abstract—To develop a new kind of composite material, 'graded morphology MMCs', a semi-solid magnesium alloy was squeeze-cast into an aluminum borate whisker preform. Currently, to increase the interfacial tensile/shear strength between MMCs and some metal parts, the joining processes have been studied. However, a suitable process has not yet been found. In this study, we first studied the optimum manufacturing condition to increase the preform compressive strength which should be necessary to prevent the preform from deformation in the squeeze cast process. The dependence of the binder types, which were the SiO_2, Al_2O_3, and TiO_2 sols, the binder content (0–5 mass% *vs* whisker amount), and the sintering temperature (1000–1160°C) of the preform were measured. We then examined the microstructure of the obtained material which was *in situ* joined with the semi-solid magnesium alloy (Mg–9 mass% Al–1 mass% Zn). The results were as follows: (1) The SiO_2 sol was the most effective as a binder to increase the preform compressive strength. (2) During the squeeze cast process, the particles of the α-Mg solid phase in the semi-solid alloy were filtered by the preform and piled up in front of the preform/semi-solid alloy interface. This causes a gradational distribution of the primary crystals in part of the obtained material.

Keywords: Squeeze casting; magnesium alloy; composites; semi-solid.

1. INTRODUCTION

Recently, semi-solid material processing has been developed. The remarkable advantages of this process are the lower amount of shrinkage cavity and smaller degree of macro-segregation in products compared with conventional casting [1–3]. From the viewpoint of composite material processing, in the current process, the

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mixing of the molten alloy and ceramics reinforcement has been difficult because of the lack of wettability between them. On the other hand, in the semi-solid process, the mechanical mixing and the uniform dispersion of the reinforcement in the metal matrix are relatively easy. Therefore, the so-called 'compo-casting process' has attracted considerable attention as a powerful process for producing MMCs. This process will be suitable for the whole reinforcement of certain components of machines. However, it is often necessary for certain components to be partially reinforced, for example, the partial reinforcement for heat-resistance in piston heads for automobiles. In this study, as a new kind of technique for partial reinforcement, the squeeze casting process of semi-solid alloy into the preform, made by the aluminum borate whisker, was examined. In order to prevent the preform from deforming during the squeeze casting process, the influence of the types of inorganic binders or sintering temperature on the compressive strength were measured. The characteristics of the obtained material made by squeeze casting were then studied.

2. EXPERIMENTAL PROCEDURE

2.1. Preparation of preform

The aluminum borate whisker, $9Al_2O_3{\cdot}2B_2O_3$ (Shikoku Kasei Co. Ltd., Alborex M12) was used for preparing the preform [4]. The characteristics of the whisker are shown in Table 1. The whisker (80 g) was dispersed in ion exchanged water (800 cc). An inorganic binder, which reinforces the preform after sintering, was then added to the water–whisker mixture. To examine the influence of the binder type on the preform compressive strength, three types of binders, SiO_2 sol, Al_2O_3 sol, and TiO_2 sol, were selected. One, 3, or 5 mass% of binders to the total weight of the whisker (80 g) was added. Both one-tenth mass% of the condensation agent (acrylic amido), which promotes the movement of the water through the filter paper, and 1 mass% of organic binder (PVA) were also added to the slurry during stirring. A uniform slurry was obtained after 10 min of stirring; then pH control was carried out in order to adhere the sol particles onto the whisker. In the case of the SiO_2 sol, the pH was controlled to 4 with aqueous acetic acid. For the Al_2O_3 and TiO_2 sols, the pH was adjusted to 11 with NH_4OH. The mixture was then slip-cast into the container which had a filter at the bottom to eliminate the water. After keeping the preform at 60°C for 24 h, the preform was sintered at a temperature of 1000, 1080,

Table 1.
Properties of aluminum borate whisker

Chemical structure	$9Al_2O_3{\cdot}2B_2O_3$
Length	10–30 μm
Diameter	0.5–1.0 μm
Young's modulus	400 GPa
Tensile strength	8 GPa

or 1160°C for 4 h. The dimensions of the obtained preform were a height of 40 mm, length of 100 mm, and width of 45 mm. The resultant volume fraction, V_f, of the whisker in the preform was about 18%.

2.2. *Preform compression test*

The compressive strength of the preform was measured at room temperature with an autograph (Shimadzu, AG-5000D). The sample preform (H35, L20, and W20) was compressed at a rate of 1 mm/min.

2.3. *Squeeze casting process*

The squeeze casting was carried out using the UBE-HV330T squeeze casting machine. The preform, which has dimensions of L100, W100, and T15, was set in the cavity of the dies as shown in Fig. 1. The semi-solid AZ91D (Mg–9 mass% Al–1 mass% Zn) alloy was prepared by heating the master billet, which was produced by rapid solidification of the molten alloy [5]. The solid fraction in the semi-solid alloy was controlled by measuring the temperature of the billet. In this study, the solid fraction of the billet, which is simply determined by the temperature of the billet according to the Mg–Al phase diagram, was set at three values: 0% (735°C), 33% (580°C), and 55% (560°C). When the temperature of the billet reached a set point, the billet was quickly inserted into the sleeve and then squeeze-cast into the cavity. In this experiment, the plunger speed was controlled

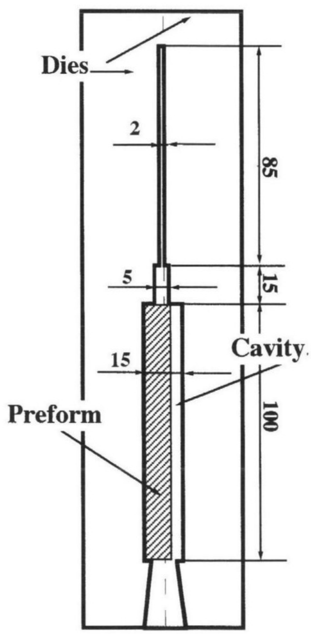

Figure 1. The dimension of dies and the location of the preform in the cavity.

so that the infiltration rate of the alloy into the preform should be 4 cm/s. The final pressure of the squeeze casting was set at 55 MPa or 100 MPa.

2.4. Characterization of the material

2.4.1. Preform. In order to investigate the surface of the whisker after sintering or the role of the sol particle as a binder for the whisker, SEM observations were carried out. TEM (Topcon-002B) and TEM-EDS (EDAX9100) analyses were also done to examine the sol particles on the whisker after sintering.

2.4.2. Composite material. An optical microscope was used to observe the microstructure of the composite material after etching with dilute nitric acid. To determine the chemical composition of the matrix in the composite, an EPMA-WDX (JEOL8900RL) analysis was carried out. To estimate the mechanical properties of the obtained material, Vickers hardness was measured on the composite part and adjoined Mg-alloy part.

3. RESULTS AND DISCUSSION

3.1. Optimization of the preform compressive strength

Figure 2 shows examples of the stress–strain curves of the compression tests. In this study, the preform compressive strength was defined as follows:

(1) If the stress–strain curve appears to have a maximum point, as shown in the SiO_2 binder, the maximum stress was adopted as the preform compression strength.

(2) In the case of the TiO_2 and Al_2O_3 binders, it was found that the preform tends to successively deform in the shape of a barrel instead of fracturing. Therefore,

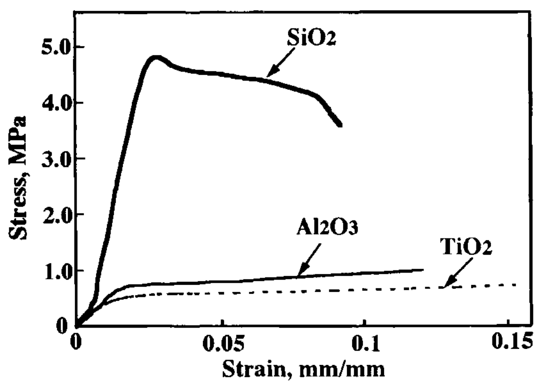

Figure 2. Stress–strain curves of the preform with 5 mass% SiO_2, Al_2O_3, or TiO_2 binder sintered at 1160°C.

if the stress simply increased with increasing strain, the stress at 5% strain was adopted as the preform compressive strength.

Figure 3 shows the influence of the binder type on the strength of the preform sintered at 1160°C. Regardless of the binder type, the preform strength tends to increase with increase in the binder content. However, it is clear that the SiO_2 sol is extremely effective for improving the preform strength compared with the other binders. The influence of the sintering temperature on the preform strength with the SiO_2 binder is shown in Fig. 4. The strength of the preform sintered at 1000°C is saturated when the binder content exceeds 3 mass%, and slightly decreased at the content of 5 mass%. On the other hand, the strength of the preform sintered at 1160°C is improved in proportion to the binder content up to 5 mass%. This reveals that the dominant factor to determine the preform strength will be the sintering temperature rather than the amount of binder. The results of the SEM observation on the surface of the whisker after sintering are shown in Fig. 5. In the case of the SiO_2 binder sintered at 1000°C, it is found that the sol particles closely cover the surface of the aluminum borate whisker. It seems that when the sintering temperature is lower than 1160°C, the amount of the particles over 3 mass% content will not work effectively, because excessive addition of the particle will bring about only the pile-

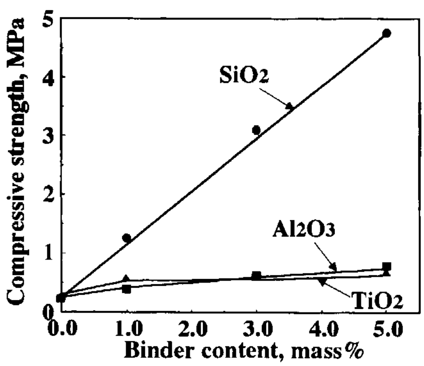

Figure 3. Influence of the binder type on the compressive strength of the preform sintered at 1160°C.

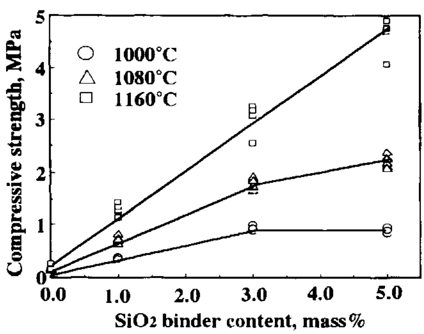

Figure 4. Influence of the sintering temperature on the preform strength with SiO_2 binder.

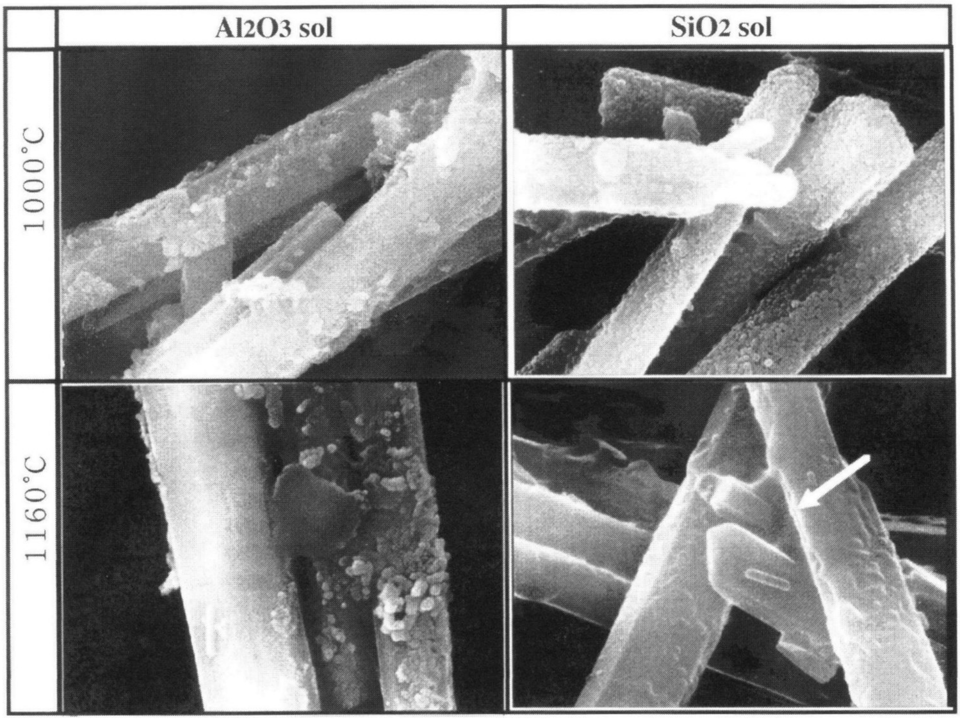

Figure 5. SEM observation of the sol particles on the whisker after sintering.

up of the sol particles on the whisker surface. This may result in the saturation of the preform strength at the binder content of 3 mass% mentioned above. On the other hand, the whisker with the SiO_2 sol sintered at 1160°C showed a very smooth surface. Although the sintering temperature is under the melting point of the SiO_2, the SiO_2 sol particles seem to melt and spread out on the surface of the whisker. As revealed by the arrow in the figure, a 'bridging' phenomenon, by which the whiskers are bound to each other, is found. This phenomenon leads to the effective improvement of the preform strength [6, 7]. As a result of the TEM observations and TEM-EDS analysis on the surface layer of the whisker (Fig. 6a), the amorphous SiO_2 phase was determined. This means that the SiO_2 sol will behave like a liquid and wet the whisker surface at the temperature of 1160°C. During the cooling process, the sol will solidify without crystallization. In the case of the Al_2O_3 binder, it is clear that the number density of the sol particles on the surface of the whisker is smaller than that of the SiO_2 sol particles. The sol particles still remain on the surface of the whisker without melting at the temperature of 1160°C and no bridging was found between the whiskers. By TEM observation and TEM-EDS analysis on the surface of the whisker (Fig. 6b), in contrast to the SiO_2 binder, many clusters of fine Al_2O_3 crystals were determined. The TiO_2 sol showed the same tendency as the Al_2O_3 sol.

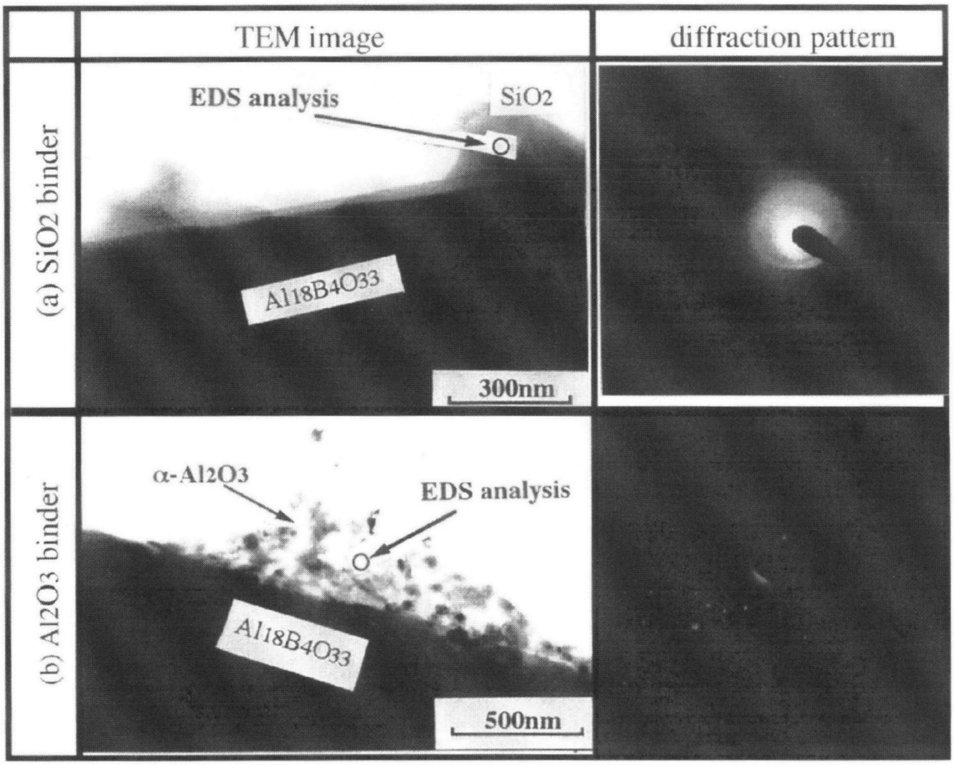

Figure 6. TEM photographs and EDS analyses of whisker in the preform sintered at 1160°C: (a) 5 mass% SiO_2 binder, (b) 5 mass% Al_2O_3 binder.

In this study, based on the above results, the preform with 5 mass% SiO_2 sol sintered at 1160°C was used in order to minimize the preform deformation in the squeeze casting of the semi-solid alloy. If the sintering temperature was set at a temperature higher than 1160°C, the bonding strength between whiskers would be improved. However, there is the possibility of damaging the mechanical properties of the whisker itself.

3.2. Characterization of the composite/alloy joined material

3.2.1. Composite part. The deformation ratio of the preform after squeeze casting was measured by observing the cross section of the products. When the molten alloy (0% solid fraction) was infiltrated into the preform by the squeeze casting, the deformation ratio was approximately 30%. However, when the solid fraction of the semi-solid alloy was 33% or 55%, 60–70% preform deformation was found. During the process of alloy infiltration into the preform, the solid phase in the semi-solid alloy, which has a diameter of nearly 100 μm, must be piled up on the surface of the preform, and then the solid phase prevents smooth infiltration of the liquid phase into the preform. This results in increasing pressure on the preform and causes large deformation of the preform.

Table 2.
Chemical compositions of the matrix in the composites and the Vickers hardness of composites (mass %)

Solid fraction	0%	33%	55%
Al	7.4	13.4	21.4
Zn	0.5	0.9	1.4
Vickers hardness (Hv)	168	313	388

The chemical compositions of the matrix in the composites, determined by EPMA point analysis, and Vickers hardness of the composites are shown in Table 2. It is found that the chemical composition in the matrix is nearly equal to the composition of the liquid phase in each specimen. For example, the equilibrium composition of the liquid phase in the 33% fs (fs, solid fraction) semi-solid alloy should be 13 mass% aluminum. This is equal to the composition determined by EPMA. Thus, it is clear that the liquid phase in the semi-solid alloy infiltrate into the preform and then solidified in the preform. Thus, the aluminum content in the preform must be increased with increasing solid fraction by phase equilibrium. This directly causes an increase in the amount of the $Al_{12}Mg_{17}$ intermetallic compound in the preform. This is one reason for the higher Vickers hardness in the higher solids fraction material. However, the increase in the volume fraction of the whisker accompanied with the preform deformation will be a primary factor for increasing the hardness of the composites.

3.2.2. Alloy/composite interface. Figure 7 shows the optical microscope images of the cross-sections of the products. As shown in the supplementary illustration of this figure, the observed section A (top) is nearer the dies. The morphology, including the alloy/composite interface, is shown in section C (Interface). Section D (composites) shows the microstructure of the aluminum borate whisker reinforced composites. As for the specimen of 0% fs, the α-Mg solid phase in the alloy slightly increases toward the alloy/composite interface; however, the typical morphology of the conventional cast AZ91D alloy is found in each section. In the case of the 33% fs specimen, the solid fraction in section C is obviously larger than that in section A. This will be caused by the pile-up of the solid phase when the semi-solid alloy infiltrates into the preform. In the 55% fs specimen, only the α-Mg phase is found in both sections B and C.

At this point, the effect of the pile-up of the solid phase at the alloy/composite interface on mechanical properties of this material should be discussed. A part of liquid phase of the AZ91D semi-solid alloy solidifies with the eutectic reaction, and the resultant phases are composed of the α-Mg phase and the $Al_{12}Mg_{17}$ intermetallic compound phase. Consequently, the α-Mg solid phase will be deformed compared with the post-liquid phase. Here, in this paper, 'the post-liquid phase' means the solidified liquid phase in the semi-solid alloy. The micro-Vickers hardness of the α-Mg solid phase and the post-liquid phase are shown in Table 3. The higher value

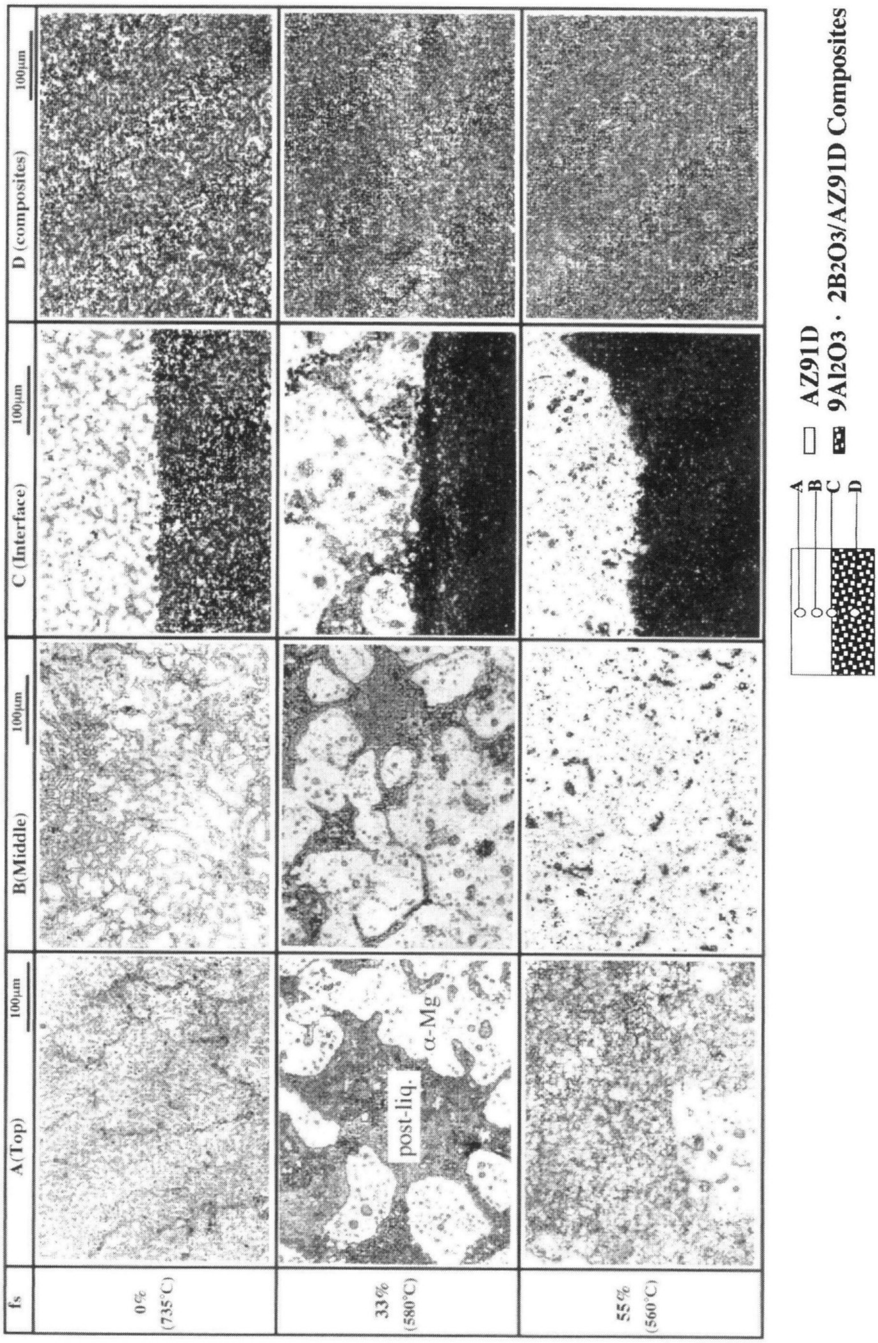

Figure 7. Optical microscope images of $9Al_2O_3{\cdot}2B_2O_3/AZ91D$ composites.

Table 3.
Vickers hardness of the solid phase and the post-liquid phase

Solid fraction (fs)	0% solid	33% p-liq.	55% solid	p-liq.	solid	p-liq.
Vickers hardness (Hv)	65	74	65	90	62	97

of the hardness for the post-liquid phase compared with the solid phase is due to the existence of the compound phase. When the tensile stress or the shear stress is given to the alloy/composite interface, it is expected that the piled up solid phase at the interface will be deformed or be elongated. This will increase the fracture toughness of the alloy/composite interface.

4. CONCLUSIONS

(1) At a suitable sintering temperature, the SiO_2 sol spreads over the surface of the whisker and bridges the whiskers. During the cooling process after sintering, the SiO_2 sol solidifies without crystallization and binds the whiskers with a smooth curved surface in the shape of a web. This leads to the effective improvement of the preform strength.

(2) In the process of squeeze casting the semi-solid AZ91D alloy into the preform, the solid phase piles up in front of the preform. A ductile α-Mg layer is then formed. This will improve the toughness of the alloy/composite interface.

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