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## Magnesium Matrix Composites: State-of the-art and what's the future

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**Abstract.** A huge number of different process types are in use to produce magnesium-based composites. Depending on the reinforcement type, all the processes can be subdivided into solid state or powder metallurgical (PM) and liquid phase or ingot metallurgical (IM) processes. In this paper we will focus on ingot metallurgy processes. These liquid state processes result quite often in a very good interface of reinforcement with the magnesium matrix. The liquid processes can be further subdivided into infiltration techniques, casting processes and spray deposition. Those are the most inexpensive processing technologies for discontinuous, reinforced magnesium-based composites. When produced using melting processes, nanoparticle-reinforced magnesium composites are expected to improve in strength, due to the grain refinement described in the Hall-Petch relation. When an isotropic distribution of nanoparticles is achieved, the composites are additionally expected to be Orowan-strengthened. That is why nanosized reinforcements are expected to represent the future for improving the properties of magnesium-based metal matrix composites.

### Kinds of Reinforcement

For the magnesium-based composites, ceramic reinforcements and carbon fibers were used, in order to study their mechanical and physical properties. Metallic particles or fibers were not included in the selection, due to their poor expected corrosion properties. It is possible to tailor the mechanical properties of the composite within a certain range by choosing the kind, the geometry, the amount and, in the case of fibers or whiskers, the geometric distribution of reinforcements. If more than one kind of reinforcement shape (particles, short fibers, whiskers or long fibers, see Fig. 1) is used, the composite is called a hybrid reinforced composite. In this case it is possible to profit from the different advantages inherent in each reinforcement type by combining them.

**Particle Reinforcement.** For the reinforcement of magnesium alloys, hard ceramic particles are usually chosen that are in use for grinding and polishing applications. Typical particle materials are nitrides (BN, AlN, TiN, ZrN), carbides (B<sub>4</sub>C, ZrC, SiC, TiC, W<sub>2</sub>C, WC), oxides (ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>) and borides (TiB<sub>2</sub>, ZrB<sub>2</sub>, WB). When choosing the reinforcement type, the chemical reactivity between the matrix of the alloy and the particles has to be taken into account. To achieve high mechanical properties, a reaction layer is necessary, because external and internal (thermal) stresses have to be transferred. Not only the kind and size of reinforcement influence the properties of the composite, but also the shape of the particles. Round, blocky and platelet forms are available. Often the platelet form is preferred, because for forming a good bonding, contact with a crystal plane may be necessary, which is possible in platelets rather than in round particles. Particles with sharp edges are usually avoided, because the edges may act as the starting points for cracks when the material is stressed. Compared to other metals, the magnesium melt is very reactive and forms reaction product layers with all these reinforcements. If the duration of contact with the melt is too long, some ceramic materials can even dissolve. In order to reach a low-density composite, the density of the reinforcement particles should be low. However, another reason for needing a good density combination is the fact that when composites are fabricated by melt-stirring processes, the differences between matrix and particle densities should be kept small, because particles would otherwise sink down or float to the top of the melt.

**Continuous Fiber Reinforcement.** Compared to the variety of particles, there are fewer materials available in continuous-fiber form, but many more different shapes, mechanical properties and suppliers to choose from on the market. Usually, either single fibers called monofilaments or multifilaments are used, the latter having hundreds or thousands of thin fibers in the range 5 to 25  $\mu\text{m}$ . For magnesium-based composites, carbon fibers are often used in R&D projects as well as in a few industrial applications [1]. This is due to its low density, high Young's modulus and tensile strength, low CTE, good thermal and electrical conductivity, high availability and resistivity against magnesium melt. Two differently processed carbon-fiber types are available: the PAN (polyacrylonitrile) fibers and the pitch fibers. Continuous long fibers based on oxides are mostly alumina based. In their use as reinforcement for magnesium alloys, they have some advantages. Alumina-based fibers offer good processing abilities, because during wetting with magnesium melt a stable spinel layer forms at the interface. All the fibers are cheap and stable in air and protective gases. They all have high strength, low CTE and a sufficiently low density. Depending on the content of  $\text{SiO}_2$  and  $\text{B}_2\text{O}_3$ , different production routes can be chosen for these fibers. With higher contents, fibers can be produced by spinning or melting, because the melting point is relatively low. Fibers approaching alumina-only content have a higher melting point and such processes are not economic. These fibers were produced by precursor technologies. Varying amounts of  $\text{SiO}_2$  lead to different mechanical properties. Without silica, the fibers consist of  $\alpha$ -alumina alone, which has a high Young's modulus and such fibers are brittle, resulting in only reduced strength. The most recent examples of continuous long fibers are SiC multifilament fibers. These fibers can be used as reinforcement for magnesium composites that are manufactured using spun polymer precursors. Based on polycarbosilane or polytitanocarbosilane fibers, these materials are transformed to ceramic fibers at  $1300^\circ\text{C}$  in a protective gas atmosphere. The resulting fibers have a thin protective layer of  $\text{SiO}_2$ , which enables good wetting with the magnesium melt. SiC fibers have a density close to  $2.5 \text{ g/cm}^3$  and a Young's modulus around 200 GPa. They are quite cheap and very stable, even at high temperatures, and similar to alumina-based fibers, they exhibit only small thermal expansion.

**Whisker Reinforcement.** Whiskers are small, needle-like single crystals with an aspect ratio of roughly 10 or more and a diameter of 1  $\mu\text{m}$ . They are processed by growing from oversaturated gases, or electrolysis from solutions or solids. Due to the manufacturing conditions, they have a very low defect density. Besides SiC and  $\text{Si}_3\text{N}_4$ , which have been used for magnesium-based composites as reinforcement,  $9\text{Al}_2\text{O}_3 \text{ X } \text{B}_2\text{O}_3$  and  $\text{K}_2\text{O X TiO}_2$  combinations are also of interest. The fact that whiskers are very thin and small has led to discussions about the health risks. They can be inhaled and do not degrade in the lung, leading to the suspicion of their being potentially carcinogenic.

**Short Fiber Reinforcement.** Concerning their reinforcing and strengthening effects, short fibers are midway between those of long fibers and particles. Whereas long-fiber reinforcement results in extremely anisotropic mechanical properties (high strength following the fiber's alignment and low strength at perpendicular vectors), particle reinforcement leads to nearly isotropic properties. By the use of short fibers it is possible to tailor the mechanical properties with determination of the amount, kind and distribution of the reinforcing fibers.

**Nano-sized Reinforcement.** Since ceramic nanoparticles or nanofibres are available and inexpensive, these types of reinforcement are also undergoing research for magnesium based composites. The reinforcement of magnesium alloys with very small ceramic particles or carbon nanotubes offers a wider range of property modulation, compared to the micro-sized ones. This is mainly due to the fact that Orowan strengthening is barely yielded by larger particles, because the inter-particle spacing and the size of the particles is too great [2]. When the materials are prepared by a metallurgical melting process, an additional strengthening by the grain refining induced by the nanoparticles may be achieved. Only very small particles can act as nuclei for solidification. For magnesium alloys, mainly SiC,  $\text{Al}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$  have been used as the reinforcement. Only a few studies have been performed on  $\text{SiO}_2$  and even carbon nanotubes [3].

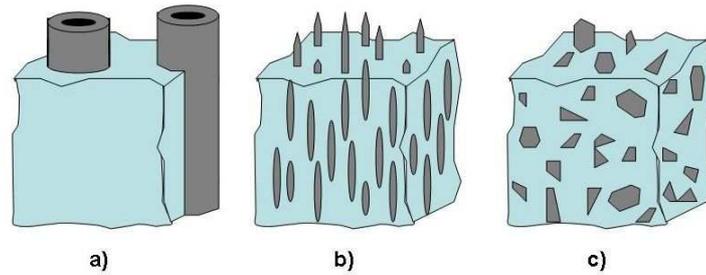


Fig. 1: Different kinds of reinforcement types: a) continuous long fibers, b) discontinuous short fibers or whiskers and c) particles in the matrix.

### Processing of Magnesium based MMCs

**Stir Casting.** The stir-casting process is the easiest and cheapest processing route to produce discontinuous, reinforced composites [4, 5]. Particles, short fibers or whiskers can be used as reinforcing components. They are introduced into the molten matrix. The force produced by stirring is needed to overcome the usually bad wetting between the matrix and reinforcement. The duration of stirring and the melt temperature strongly influences the development of an interface between the components. A heated crucible maintains the temperature during stirring. A sketch of the process is given in Fig. 2a. The reinforcement (1) is added into the melt (7). The crucible (3) is embedded in a vacuum chamber (4). In the heated crucible (2) the impeller rotates and both a horizontal and a vertical vortex are created that deagglomerate the reinforcement and distribute it homogeneously. The use of a slight vacuum prevents the materials from forming gas entrapments or a gas boundary layer on top of the melt.

**Compocasting.** Whereas the stir-casting process is performed at temperatures above the liquidus temperature of the magnesium alloys, compocasting is done between solidus and liquidus temperature. This semi-solid material, where an already solidified fraction is surrounded by liquid, is called slurry. When the slurry is sheared at high rates the viscosity decreases. Without any introduction of reinforcement, this casting process is called rheocasting. With an addition of reinforcements the process is called compocasting. The shearing forces are larger compared to stir-casting, because additional solid fractions of the magnesium alloy positively influence the rheological behaviour of the mixture. The deagglomeration, wetting and homogenisation are all improved. Three additional advantages over stir casting can be seen: (i) the temperature is lower and the semi-solid state has a much lesser tendency to burn, (ii) due to the higher viscosity of the semi-solid compared to the pure solid, the tendency of a settling of the reinforcement is reduced. Neither swimming to the top nor sinking to the bottom of the crucible takes place. Finally, (iii) due to the lower temperature, the degradation probability of the reinforcements is reduced. After distributing the reinforcement in the semi-solid, the slurry can be cast using die casting, centrifugal casting, mould casting or squeeze casting.

**Melt Infiltration Casting.** The melt infiltration casting or squeeze casting process is widely used for the manufacture of fibre-reinforced magnesium composites. Prefabricated preforms containing fibres, and where required particles, are stuck together with high-temperature stable binders (silica) and have a defined volume fraction of reinforcement. This fraction is usually between 10 and 60 vol.-%. Most often it has a volume content of 15-25 vol.-% reinforcement. Due to the manufacturing process of these preforms, the fibres are frequently not randomly oriented; rather they have a planar isotropic distribution. A sketch of the squeeze casting process is shown in Fig. 2b. The heated preforms (4) are put in a preheated mould (6) and the superheated melt is poured over it (5). The melt is squeezed into the preform by a hydraulic ram (3). After full infiltration, the part solidifies under pressure and is taken out by an ejector (1). Due to the non-turbulent flow and solidification under pressure, the castings are free of pores and blowholes, show no shrinkage porosity and have a fine-grained microstructure. One disadvantage is the possibility of damaging the preform during the early stages of infiltration. This process allows manufacturing of completely reinforced MMCs and parts with selectively reinforced areas.

**Gas Pressure assisted Infiltration Casting.** Similar to the squeeze casting process, gas pressure infiltration needs prefabricated preforms for producing composite materials. Instead of a ram, gas pressure on the melt surface is used for infiltration into the heated preform. The time taken for total infiltration in the gas pressure process is much longer compared to squeeze casting. This is important to know, because the formation of interfaces between matrix melt and reinforcement depends strongly on the time of melt contact. Often a vacuum is applied to the mold and preform, and the gas applied is usually an inert gas, such as argon.

**Ultrasound-assisted casting.** This process is used for introducing nanoparticles into the magnesium melt. The customary stir casting or infiltration casting has to be enhanced by an ultrasonic generator. An ultrasonic sonotrode is dipped in the molten alloy and the added particles are distributed with a power level of between 1.5 and 3.5 kW. Usually a frequency of 20 kHz is used for this process. Ultrasound is also needed for deagglomeration and distribution of the nanosized particles, because their high surface energy, compared to microsized particles, makes it impossible to distribute them simply by stirring. After deagglomeration the melt can be cast using a variety of techniques.

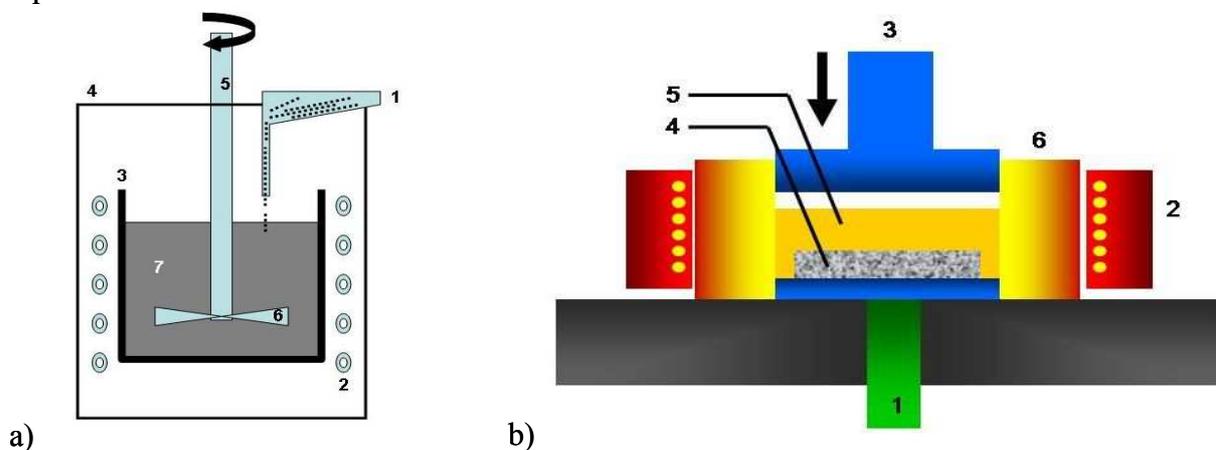


Fig. 2: Sketch of a) the stir casting process and b) the squeeze casting process

## Summary

Magnesium-based metal matrix composites show a wide range of possibilities to fit mechanical and physical properties to the intended application. With a variation of amount, distribution and kind of ceramic reinforcement, the properties can be adjusted to the surrounding materials, which may be aluminum, steel or even polymer. Mechanical properties are comparable to high-strength aluminum alloys, but magnesium-based composites show a lower density when compared to those. Whereas microsized reinforcement was investigated for some time, nanoparticles and CNTs are now the main focus of interest. They promise the best improvement of properties.

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