Influence of micro- and nanoparticles on mechanical properties of magnesium and magnesium alloys

Z Trojanová¹²*, P Lukáč¹² and J Džugan²

¹Charles University, Faculty of Mathematics and Physics, Ke Karlovu 3, 121 16 Praha 2, Czech Republic
²COMTES FHT, Průmyslová 995, 223 41 Dobřany, Czech Republic
*ztrojan@met.mff.cuni.cz

Abstract. Magnesium and magnesium alloys were reinforced with various micro- and nanoparticles (SiC, Inconel718, Al₂O₃, ZrO₂, BN, graphite) Composites were prepared by squeeze casting and using powder metallurgy followed by hot extrusion. Tensile and compression tests were performed at elevated temperatures up to 300 °C. The influence of micro- and nanoparticles on mechanical characteristics is discussed on the base of physical models. Bonding at the interface between particles and magnesium matrix plays an important role for the resulting composite properties.

1 Introduction
Metal matrix composites (MMCs), metals, and alloys reinforced with particles, fibres, platelets, or whiskers with different physical and chemical properties are intensively studied in the last two decades. If at least one size of the reinforcing phase is in the micrometer range, we deal with the metal matrix microcomposite (mMMS) or if it exhibits a size up to 100 nm, this is a metal matrix nanocomposite (nMMC). Magnesium and magnesium alloys reinforced with various micro- and nanoparticles (mp and np) are very attractive materials with improved mechanical properties. The specific stiffness and strength are better compared to the monolithic materials, whereas the low density is preserved. Magnesium based MMCs usually have limited ductility. The strengthening of MMCs is a complex problem. Various mechanisms responsible for the strengthening of MMCs are described in the literature [1-4]. The problem how to combine the individual strengthening terms was not up to now satisfactorily solved. In the present study, the mechanical characteristics of magnesium-based mMMCs and nMMCs, prepared with different methods, are presented. Various strengthening mechanisms are discussed with the aim to find the main effects decided by the composites’ resultant properties.

2 Manufacturing methods
The main problem in the manufacturing of MMCs is the uniform distribution of reinforcing phase particles or fibres in the metallic matrix. For composites preparation methods in situ where particles are formed in the melt solidification via a chemical reaction, or ex situ where the ready particles are inserted into the molten matrix. Usually, simple mixing of both phases is not an effective method due to the low wettability of particles or their tendency to form clusters. One possibility, how to avoid this problem, is using a prefabricated preform – some structure containing particles and a binder. The metallic melt is pressed into the preform in the squeeze casting process. In many cases, powder metallurgical methods
are utilized for the manufacturing of mMMCs or nMMCs. In this case, the metallic powder is mixed with the particles, then compacted and hot extruded. The milling of powders with particles is often used for a better distribution of particles in the matrix. The original technique for the preparation of mMMCs and nMMCs was developed by Gupta and coworkers [1]. In the disintegration melt deposition (DMD) method, the melt containing the particles is disintegrated by the Ar current and then compacted and hot extruded. While MMCs prepared using squeeze casting exhibit no preferential orientation, the MMCs manufactured by the powder metallurgical (PM) methods exhibit some texture. This texture is the reason for the often observed tension compression anisotropy of magnesium extruded materials [5]. In textured Mg materials, the basal planes are parallel to the extrusion direction (ED) (the $<$c$>$ axis is perpendicular to the ED), while the majority of the prismatic planes rotate around the $<$c$>$ axis.

3 Mechanical properties

3.1 Microcomposites manufactured using a preform.

A commercially available AZ91 (Mg – 9%Al; 1%Zn; 0.3%Mn) was reinforced with 10 vol.% of SiC particles and an addition of 3wt% of Si. Composites were prepared by the squeeze casting method using a preform. The microstructure consists of SiC particles, $\delta$-Mg grains (solid solution of Al in Mg), primarily segregated $\gamma$-phase ($\text{Mg}_{17}\text{Al}_{12}$) and discontinuous precipitates (lamellae of $\gamma+\delta$ phase). The addition of 3%Si gives rise to the $\text{Mg}_{2}\text{Si}$ phase. Details of the microstructure are visible in the scanning electron micrograph introduced in Figures 1a,b,c, and d. Similar preform containing SiC particles and an addition of C was used for the mMMC based on ZE41 alloy (Mg – 4%Zn – 1%RE). The tensile yield stress (TYS) and ultimate tensile strength (UTS) estimated for both composites at various temperatures are reported in Table 1. For comparison, the values of characteristic stresses obtained for the monolithic alloys are shown. The reinforcing effect of particles decreases with increasing temperature.

![Figure 1](image-url)

Figure 1. Details of microstructure visible in electron micrographs: a) $\text{Mg}_{2}\text{Si}$ eutectics in the form of Chinese script; b) $\text{Mg}_{17}\text{Al}_{12}$ continuous and discontinued precipitates; c) and d) $\text{Mg}_{2}\text{Si}$ and SiC particles.

| Table 1. Mechanical characteristics of mMMCs based on Mg alloys investigated in tension. |
|-----------------------------------------------|
| T ($^\circ$C) | TYS (MPa) | UTS (MPa) | TYS (MPa) | UTS (MPa) | TYS (MPa) | UTS (MPa) | TYS (MPa) | UTS (MPa) |
| 23 | 175 | 359 | 183 | 394 | 141 | 237 | 122 | 264 |
| 50 | 182 | 328 | | | | | | |
| 61 | | | | | 138 | 237 | | |
| 100 | 146 | 337 | 164 | 328 | 132 | 208 | 89 | 213 |
| 150 | 132 | 237 | 136 | 222 | 108 | 166 | 114 | 230 |
| 200 | 105 | 141 | 89 | 139 | 102 | 122 | 104 | 188 |
| 250 | 82 | 98 | 78 | 91 | 78 | 91 | 97 | 161 |
| 300 | 53 | 57 | 57 | 66 | 57 | 66 | 67 | 92 |

3.2 Microcomposites prepared by the powder metallurgical technology
Two mMMCs were prepared by mixing, compaction, and hot extrusion of the powders. Figure 2a shows the light micrograph of the as-prepared WE54+13vol%SiC mMMC. The SiC particles having a size of several µm are not uniformly distributed in the matrix; they form in many cases clusters. A significant amount of cuboidal fine particles (20-40 nm) was estimated distributed inside of the grains. On the basis of electron diffraction patterns, the particles were attributed to the $\beta'\text{Mg}_{12}\text{NdY}$ phase. Another feature in the microstructure is a significant increase of the dislocation density visible in the left bottom corner in Figure 2c.

![Micrographs of WE54/SiC mMMC](image)

**Table 2.** Mechanical characteristics of two mMMCs prepared with PM technology.

| T (°C) | CYS WE54+13%SiC (MPa) | CPS WE54+13%SiC (MPa) | CYS Mg-8Li+7%SiC (MPa) | CPS Mg-8Li+7%SiC (MPa) | CYS WE54 (MPa) | CPS WE54 (MPa) | CYS Mg-8Li (MPa) | CPS Mg-8Li (MPa) |
|-------|-----------------|-----------------|-----------------|-----------------|----------------|----------------|----------------|----------------|
| 23    | 246             | 370             | 198             | 405             | 141           | 274           | 85             | 171           |
| 50    | 241             | 361             | 187             | 390             | 146           | 289           | 90             | 144           |
| 100   | 226             | 348             | 166             | 284             | 148           | 271           | 52             | 81            |
| 150   | 220             | 327             | 127             | 159             | 136           | 262           |                 |               |
| 200   | 217             | 305             | 74              | 83              | 123           | 250           | 41             | 60            |
| 250   | 168             | 227             | 35              | 40              | 114           | 261           |                 |               |
| 300   | 65              | 82              | 15              | 22              |               |               |                 |               |

Similarly, the SiC particles were nonuniform distributed in the Mg-8Li alloy. This alloy is consisted of two phases: HCP $\alpha$ phase and BCC $\beta$ phase. The compression yield strength (CYS) and compression peak stress (CPS) measured for two magnesium alloys and the unreinforced alloys are reported in Table 2. The reinforcing influence of particles is really high. Note that the values introduced in Table 2 for unreinforced alloys were obtained for cast alloys.

3.3 Microcomposites prepared by disintegrated melt deposition.

Pure magnesium reinforced with 0.7, 1.4, and 2.4 vol% of Inconel 718 particles was prepared using DMD technique. Magnesium melt together with the Inconel powder (0.2-5 µm) was disintegrated by the Ar gas before being deposited onto a metallic substrate [4]. Processed ingots were hot homogenised and hot extruded. Samples were deformed in tension and compression at elevated temperatures. Characteristic stresses are reported in Table 3 together with the stresses measured for pure Mg, prepared with the same method. Pronounced tension-compression asymmetry is appreciable. Such asymmetry is done by the basal texture which was formed in the extrusion process. The high reinforcing effect of In718 microparticles is obvious from Table 3 even by the small volume fraction of particles.
Table 3. Mechanical characteristics found for Mg-In718 mMMCs deformed in tension and compression.

| T °C | 0.7 vol% | 1.4 vol% | 2.4 vol% | 0.7 vol% | 1.4 vol% | 2.4 vol% |
|------|----------|----------|----------|----------|----------|----------|
| 23   | 161      | 207      | 249      | 285      | 260      | 301      | 339 |
| 100  | 98       | 156      | 163      | 157      | 173      | 250      | 247 | 255 |
| 200  | 42       | 113      | 95       | 113      | 78       | 211      | 215 | 211 |
| 300  | 21       | 47       | 51       | 48       | 35       | 61       | 61  | 61  |

CYS (MPa)       CPS (MPa)
23  88   131  152  185  383  295  326  362
100 91   122  154  196  241  239  280  313
200 69   109  112  139  103  153  168  183
300 34   41   108  70   40   48   137  78

3.4 Nanocomposites prepared by milling and powder metallurgy.
Magnesium was reinforced with ceramic np (Al₂O₃, ZrO₂, BN) and graphite via PM technology. Powders were mixed and milled together, compacted and hot extruded. TEM showed particles of Al₂O₃ and ZrO₂ in the grain boundaries and some particles were found inside of grains. In the case of nMMCs with hexagonal BN (hBN) and Gr, the nanoparticles remained in the grain boundaries (see figure 3). Particles of hBN have a similar layered structure as Gr, within each layer, boron and nitrogen atoms are bound by strong covalent bonds, whereas the layers are held together by the weak van der Waals forces. The fine BN and Gr nanoparticles deformed during the milling and created intergrain material layers.

Table 4. Mechanical characteristics of Mg/Al₂O₃ and Mg/ZrO₂ obtained in tension and compression.

| T (°C) | µMg TYS (MPa) | µMg UTS (MPa) | Mg+3Al₂O₃ TYS (MPa) | Mg+3Al₂O₃ UTS (MPa) | Mg+3ZrO₂ TYS (MPa) | Mg+3ZrO₂ UTS (MPa) | CYS (MPa) | CPS (MPa) |
|--------|---------------|----------------|---------------------|---------------------|---------------------|---------------------|-----------|-----------|
| 22     | 229           | 257            | 269                 | 306                 | 176                 | 208                 | 189       | 415       | 162       | 236       |
| 77     | 171           | 186            |                     |                     |                     |                     |           |           |           |           |
| 100    |               |                |                     |                     |                     |                     |           |           |           |           |
| 126    |               |                |                     |                     |                     |                     |           |           |           |           |
| 200    | 78            | 85             | 86                  | 91                  | 68                  | 73                  | 96        | 111       | 80        | 85        |
| 300    | 49            | 54             | 50                  | 51                  |                     |                     |           |           |           |           |

Table 5. Mechanical characteristics of µMg and µMg+3vol%BN.

| T (°C) | µMg TYS (MPa) | µMg compression | Mg+3BN TYS (MPa) | Mg+3BN UTS (MPa) | CYS (MPa) | CPS (MPa) |
|--------|---------------|-----------------|------------------|------------------|-----------|-----------|
| 22     | 254           | 284             | 229              | 317              | >450      | 339       | 406       |
| 100    | 162           | 175             | 158              | 170              | 447       | 485       | 310       | 325       |
| 200    | 67            | 82              | 90               | 93               | 157       | 191       | 125       | 131       |
| 300    | 34            | 40              | 47               | 62               | 77        | 79        | 76        | 78        |

Samples with ceramic np were deformed in tension and compression at temperatures from RT up to 300 °C. The characteristic stresses obtained at various temperatures are reported in Table 4 together with the values for pure Mg, prepared with the same technique. Tension compression asymmetry is obvious at RT and 100 °C. The characteristic stresses found in tension and compression for Mg with 3 vol% of BN
np are shown in Table 5. Note that the powder of pure Mg was only compacted and extruded (not milled) in contrast to the Mg+3vol%BN nanocomposite. The same preparation technology as in the case Mg/BN nMMC of Mg with Gr nanoparticles. Pure Mg was in this case milled and therefore the grain size of Mg samples was about 150 nm. Samples with Gr np were deformed in compression at RT and temperatures higher up to 300 °C. Comparing the YS measured for magnesium nMMCs with various np, we may state that Gr and hBN are materials with the excellent reinforcing effect (see Table 6).

Table 6. Mechanical characteristics of UFG-Mg and UFGMg+3vol.%Gr.

| T (°C) | YS (MPa) | CPS (MPa) | YS (MPa) | CPS (MPa) |
|-------|----------|-----------|----------|-----------|
| 22    | 222      | 336       | 259      | 293       |
| 50    | 209      | 300       |          |           |
| 77    |          |           | 196      | 212       |
| 100   | 170      | 208       |          |           |
| 150   | 124      | 135       |          |           |
| 200   | 90       | 96        | 149      | 158       |
| 250   | 60       | 76        |          |           |
| 300   | 60       | 68        | 111      | 129       |

4 Strengthening mechanisms

Speaking about the strengthening mechanisms in MMCs, many mechanisms must be considered: load transfer from the matrix to reinforcing phase particles (or fibres), increased density of thermal and geometrically necessary dislocations, Hall-Petch strengthening, and the influence of residual thermal stresses [4]. The special problem is how to combine the individual strengthening mechanisms. The particular strengthening terms expressed on the base of the physical models are summarised in Table 7.

Table 7. Contributions to strengthening following from the presence of the reinforcing phase.

| Mechanism       | Relationship                                                                 | Symbols |
|-----------------|------------------------------------------------------------------------------|---------|
| Load transfer   | \( \Delta \sigma_L = 0.5\sigma_A f \)                                      | \( \sigma_A \) alloy stress, \( f \) vol% of particles |
| Density of thermal dislocations | \( \rho_T = 12f\Delta \alpha \Delta T/b(1-f)s \)                      | \( \Delta \alpha \Delta T \) thermal strain, \( b \) Burgers vector, \( s \) size of particles |
| Enhanced dislocation density | \( \Delta \sigma_D = \alpha_y G \beta (\rho_T + \rho_p)/s \)         | \( \rho_p \) plastic strain |
| Density of geometrical dislocations | \( \rho_g = f\rho_s b \)                                       | \( \rho_s \) plastic strain |
| Orowan strengthening | \( \Delta \sigma_{OR} = \frac{G \beta}{\Lambda} \left( \frac{5}{2\pi} \right) G \epsilon_p \) | \( G \) shear modulus, \( \Lambda \) distance between particles |
| Residual stresses | \( \sigma_{TS} = \frac{2}{3} \sigma_y ln \left( \frac{1}{f} \right) \frac{f}{1-f} \) | \( \sigma_y \) yield stress in the matrix |
| Hall-Petch strengthening | \( \Delta \sigma_{GS} = K_y \left( d_2^{-1/2} - d_1^{-1/2} \right) \) | \( K_y \) Hall-Petch constant, \( d \) grain size |

The contribution to the strengthening from various mechanisms may be calculated according to the equations introduced in Table 7. The problem is how to combine individual strengthening terms. Possible solutions will be demonstrated in two examples. In the first, the strengthening effect of microparticles in Mg+2.4%In718 mMMC is calculated [6]. The simplest possibility is the plain summation of all contributions. The strengthening effect of mp, \( \Delta \sigma_C \) calculated for the composite
deformed in tension $\Delta \sigma_{(sum)} = \sigma_t - \sigma_y = \Delta \sigma_{p} + \Delta \sigma_{H} + \Delta \sigma_{TT} + \Delta \sigma_{DR} + \Delta \sigma_{TS} = 33.2 + 84.2 + 2 + 2 + 10 = 131.4$ (in MPa). The experimental value $\Delta \sigma_{(exp)} = 285 - 161 = 124$ MPa. The obtained result may be thought as a reasonable estimation, knowing that the particles have no unified size and are not evenly distributed in the matrix. The second possibility how to calculate the reinforcing contribution of particles, also mentioned in the literature, is the square root of quadrats of the strengthening terms.

$$\Delta \sigma_C(SR) = (\Delta \sigma_{p}^2 + \Delta \sigma_{H}^2 + \Delta \sigma_{TT}^2 + \Delta \sigma_{DR}^2 + \Delta \sigma_{TS}^2)^{1/2}.$$ The calculation gives for $\Delta \sigma_C(SR)$ a smaller value of 91.1 MPa. In the second example, the reinforcing effect of 13 vol% SiC mp is estimated: $\Delta \sigma_{(sum)} = 28 + 52 + 11 + 4 + 28 = 123$ and $\Delta \sigma_{(SR)} = 66.4$ (in MPa). The experimental value exhibits $\Delta \sigma_{(exp)} = 105$ MPa. Comparing both results, the simple sum of all contributions seems to be the better solution. The strengthening effect of nanoparticles is much lower. In the case of Mg+3vol%Al2O3 and Mg+3vol.%Gr, it exhibits only about 40 MPa. It is remarkable that the TYS of Mg+3vol% of ZrO2 is lower compared with pure Mg. The difference between TYS(Mg+3Al2O3) - TYS(Mg+3ZrO2) = 93 MPa and CYS(Mg+3Al2O3) - CYS(Mg+3ZrO2) = 27 MPa. For such differences, there is no explanation on the base of the model presented above. This problem may be solved using internal friction (IF) measurements. While the IF, characterised by the logarithmic decrement, exhibits for Mg+3Al2O3 IF = 0.0126 (at the strain amplitude $\sim 10^{-5}\) , the IF value estimated for Mg+3ZrO2 is approximately ten times higher IF = 0.0128. The high values of IF are measured due to boundary sliding in the Mg/ZrO2 interface. The bonding is weak in this case. On the other hand, nearly perfect bonding between Mg and Al2O3 may be considered. This strong bonding is caused by the chemical reaction: $3\text{Mg} + \text{Al}_2\text{O}_3 \rightarrow 3\text{MgO} + 2\text{Al}$. Similar reaction can be written for SiC particles: $2\text{Mg} + \text{SiC} \rightarrow \text{Mg}_2\text{Si} + \text{C}$. An evidence of this reaction is visible in Figure 1d, where the interface between the SiC particles and the matrix is not smooth; it is decorated with a new compound which is a result of the chemical reaction of C coming from SiC particles with Al present in the $\delta$-solid solution.

5 Conclusions
Magnesium and magnesium alloys based micro- and nanocomposites, prepared with different technologies were deformed in tension and compression in the temperature range from room temperature up to 300 °C. The reinforcing effect of particles strongly depends on the manufacturing process. The incorporated particles refined the grain size and contributed to an improvement of mechanical properties due to the Hall-Petch strengthening. An increase in the dislocation density plays also an important role in the composites strengthening. The grain boundaries and bonding between particles and the metallic matrix are deciding for the resultant composite properties.

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