Effect of hexagonal boron nitride and graphite nanoparticles on the mechanical and physical properties of magnesium

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Abstract. Magnesium nanocomposites reinforced with 3 vol.% of hexagonal boron nitride (hBN) and ultrafine-grained magnesium with 3 vol.% of graphite (Gr) nanoparticles were prepared by milling followed by hot extrusion. The influence of the hBN and Gr nanoparticles on the mechanical and physical properties of magnesium were subsequently investigated. The microstructure of the nanocomposites was analysed by electron microscopy. The nanocomposites were deformed in compression over a wide temperature range from room temperature to 300 °C and true stress-true strain curves were determined. The linear thermal expansion coefficient was measured over a wide temperature range from room temperature up to 400 °C. Pre-deformation in compression was used to estimate the influence of twins on the thermal expansion coefficient. The results are analysed and possible physical mechanisms for the observed mechanical and physical properties are discussed.

1. Introduction

Wrought magnesium and magnesium alloys have recently been the focus of researchers working with extruded and rolled materials. Such materials exhibit a finer microstructure and better mechanical properties in comparison with cast materials. A further possibility for improvement of mechanical properties is the preparation of composite materials with a reinforcing phase having different physical and mechanical properties [1-8]. The resulting properties of such composites can be tailored according to the requirements of the technical praxis. If the size of the reinforcing phase particles or fibres extends down to the nanometer region (1-100 nm) it is possible to speak about nanocomposites. Nanocomposites based on magnesium or magnesium alloys have significant advantages including very good mechanical properties. The reinforcing phase content is usually lower than 5 vol.%. The disadvantages of magnesium nanocomposites are mainly the complicated and expensive preparation techniques, and the anisotropy of these materials. This anisotropy arises from the anisotropy of the hexagonal close packed magnesium crystal structure (hcp) with consequences for both mechanical and physical properties [9].

Magnesium-based composites prepared with various amounts of nanoparticles have been studied by several authors [6]. The resulting properties of such nanocomposites depend on volume fraction of the...
reinforcing phase particles, their mechanical, physical and chemical properties and the distribution of particles in the matrix. An important role is also played by the bonding between the nanoparticles and magnesium matrix [10]. Hexagonal boron nitride (hBN) ceramics and graphite exhibit a similar layered structure in which atoms within each layer (C, and B with N) are bound by strong covalent bonds, whereas the layers are held together only by weak van der Waals forces. Both (Gr and hBN) have high melting point ($T_m$(Gr)=$3642$ °C, $T_m$(hBN)=$2973$ °C) and low density ($\rho$(Gr)=$2.2\times10^3$ kgm$^{-3}$, $\rho$(hBN)=$2.1\times10^3$ kgm$^{-3}$). Both nanoparticles should act as sliding layers as well as diffusion barriers in metal matrix composites [15]. In spite of several attempts there is no satisfying model describing the mechanical and physical properties of nanocomposites. This is due in part to the complex nature of this problem, including many factors which influence the nanocomposites behaviour. In the paper we contribute to the solving of this problem by comparing the mechanical and physical properties of two magnesium nanocomposites reinforced with particles of similar structure.

2. Experimental procedure

Nanocomposites were prepared by the powder metallurgical route. Microcrystalline magnesium was used as a matrix for the nanocomposites. Hexagonal boron-nitride or graphite nanoparticles were used as a reinforcement phase.

The first nanocomposite – ultrafine-grained (UFG) magnesium containing 3 vol.% of graphite nanoparticles (UFG-Mg+3nGr) – was obtained using Mg powder prepared by gas atomization of a high purity magnesium melt, in an argon atmosphere containing 1% of oxygen for powder passivation. The mean particle diameter was approximately 40 µm. The graphite powder used had a median particle size of 1-2 µm. The Mg powder was mixed with 3 vol.% of graphite powder in an asymmetrically moving mixer for 8 h. Afterwards the powder mixtures were milled for 8 h at 200 rpm in a planetary ball mill (Retsch, PM 400) in a sealed argon atmosphere. The milling vessel of 500 ml volume was made of corundum ($\text{Al}_2\text{O}_3$) and the milling balls (11 mm diameter) were made of hardened steel (100Cr6). The ball-to-powder weight ratio was 10:1. The composite was encapsulated in an evacuated Mg container (70 mm in diameter), degassed at 350 °C, and extruded at the same temperature with a 400 ton horizontal extrusion press (Collin 630t, extrusion die, 14 mm outlet diameter). Analyses of the extruded material in a light spark analyser (Spectrolab, Spectro Analytical Instruments) revealed no contamination of the composite by elements such as Fe from the extruder tools or milling balls, or Al from the milling vessel [8]. The mean grain size of specimens was estimated, using transmission electron microscopy and X-ray profile analysis, to be about 200 nm.

The second nanocomposite – UFG magnesium with 3 vol.% of BN nanoparticles (UFG-Mg+3nBN) – was prepared by ball milling of commercially available magnesium powder with 45 µm mean particle size, mixed and milled together with hexagonal boron nitride nanoparticles of 500 nm mean particle size in a planetary ball mill (Retsch, PM 400) under air atmosphere. A corundum-coated steel milling cup with a volume of 500 ml was filled with the powder mixture and 7 mm diameter and 13 mm diameter light corundum balls. The ratio of the mass of powder, the 7 mm balls and the 13 mm balls was 1:1.5:1.5. The powder volume in the milling cup, being about 20% of the whole volume, was milled for 6 h at 150-200 rpm. Oxidation, plastic deformation, and fracture of the magnesium powder particles took place during the milling. The graphite-like structure of the fine hBN nanoparticles was deformed during the milling and created inter-grain material layers. The milled powder was filled into aluminium capsules of 70 mm diameter, 2 mm wall thickness, and about 220 mm height, closed at one end with a circular plate of 5 mm thickness. The powder was multistage cold pre-pressed at a pressure of 65 MPa. The capsules were repeatedly filled to about one half of the remaining height after successively pressings up to 210 mm height of the pressed powder. Afterwards the capsule was closed by another circular plate of 5 mm thickness with a small hole of 2 mm diameter in the middle with fitting threads in the capsules and plates. The small hole acted as gas outlet during hot extrusion. The pre-compact samples were hot extruded to rods of 12 mm diameter (1:5.8 extrusion ratio) using a horizontal 630 t hot extrusion press. The extrusion temperature and speed were 350 °C and 1.5 mm/s, respectively.
The texture of the samples was studied using a FEI Quanta 200 FX scanning electron microscope equipped with an EDAX electron backscatter diffraction (EBSD) camera. Orientation imaging microscopy (OIM) software was utilized to analyze the EBSD data sets. The grain size was estimated in the planes perpendicular to the extrusion direction to be about 600 nm.

Specimens were deformed in compression in an Instron machine in the temperature range from room temperature to 300 °C at a constant crosshead speed, giving an initial strain rate in the order of $10^{-3}$ s$^{-1}$. True stress-true strain curves were obtained from the measurements. Characteristic stresses – compression yield stress (CYS) and ultimate compression strength (UCS) were estimated from the stress-strain curves.

Specimens for transmission electron microscopy (TEM) analysis were prepared by cutting slices from the center of compression test specimens with diameter of 3 mm and thickness of 0.8 mm. These slices were ground and then dimpled to about 15 µm thickness in the center. The final step of the specimen preparation was ion milling using a precision ion polishing system (Gatan 691) under conditions of 4.5 kV and an incident angle of 4 - 3.5°. The specimens were examined using a Philips CM12 transmission electron microscope operated at 120 kV.

The linear thermal expansion of specimens was measured in an argon protection atmosphere using a Netzsch 410 dilatometer, over a temperature range from RT up to 400 °C. Four temperature cycles (heating-cooling) were performed using heating and cooling rates of 0.9 K/min.

The Young’s modulus was measured using a resonant frequency and damping analyser (RFDA). Samples were excited to vibrations in the resonant frequency using a small striker. Free vibrations of the sample were registered with a microphone and a fast Fourier transform was used for estimation of the resonant frequency.

3. Results and discussion

True stress-true strain curves obtained for UFG-Mg+3nGr and UFG-Mg+3nBN are given in figures 1a and 1b. Characteristic features of the curves are the small local maxima observed at the beginning of the curves at RT and at 100 °C. Such a small maxima is usually observed in deformation curves of magnesium samples exhibiting a basal texture prepared by hot extrusion [11].

![Figure 1](image.png)

**Figure 1.** True stress-true strain curves determined at various temperatures in compression for UFG-Mg+3nGr (a) and UFG-Mg+3nBN (b).

The temperature dependency of the compression yield stress (CYS) and the ultimate compression stress (UCS) are shown in figures 2a and 2b. The stress (CYS and UCS) required for deformation at RT and 100 °C are much higher for the nanocomposite containing BN particles than for the composite reinforced by Gr nanoparticles. Both characteristic stresses decrease with increasing deformation temperature. This increase is stronger for the nanocomposite containing BN nanoparticles. At 200 °C
and 300 °C both the CYS and UCS are higher for UFG-Mg+3nGr, providing evidence for the better thermal stability of the composite with Gr. The plasticity of UFG-Mg+3nBN sample is very low at RT, but increases to comparable amounts in both materials at elevated temperatures. The highest plasticity was estimated for both materials at 200 °C. Such behaviours were observed in other magnesium composites [11]. The main glide system in polycrystalline hexagonal magnesium alloys and composites is basal slip of <a> dislocations with Burgers vector of 1/3[11̅2] on the (0001) basal planes. According to the von Mises criterion, the activity of five independent slip systems is necessary for a general compatible deformation [12]. However for basal slip in magnesium only two systems are independent. The Von Mises condition may be fulfilled by the additional slip of <a> dislocations in prismatic systems or by activity <c+a> dislocations with a Burgers vector of 1/3 [1123] in non-basal slip systems (prismatic or pyramidal). In magnesium several potential twinning systems may also be found, among which the {101̅2} (101̅1) twinning system is most often observed.

![Figure 2](image1.png)

**(Figure 2.** Dependence of mechanical properties on temperature for both nanocomposites: (a) compression yield stress, CYS, and (b) ultimate compression strength, UCS.)

Hexagonal magnesium materials prepared with the hot extrusion technique exhibit a pronounced texture with the basal planes parallel to the extrusion direction. Such a fibre texture was found also in UFG-Mg+3nBN, as shown in figure 3. Texture of magnesium reinforced with BN particulates synthesised using microwave-assisted sintering technique, were studied by Seetharaman and co-workers [13]. They estimated weakening of the formed basal texture with an increase in nano BN particles.

![Figure 3](image2.png)

**(Figure 3.** Basal texture of the as-extruded UFG-Mg+nBN nanocomposite.)
Preferential orientation of the basal planes in the extrusion direction does not allow deformation by twinning during tensile deformation. However, tensile twins are activated during compression experiment along $<0001>$ where the Schmid factor for twinning is high. Such twinning causes a misorientation of $86.3^\circ$ between the twinned and the untwinned lattice [14], as shown schematically in figure 4. Twinning deformation is exhausted after a plastic strain of several percent, and further deformation continues with dislocation activity in the reoriented grains [15]. New twin boundaries can act as obstacles for dislocation motion and therefore rapid hardening may be observed. The twinning mechanism is not a thermally activated process whereas dislocation motion depends strongly on the temperature. At higher temperatures the critical resolved shear stress for $<c+a>$ dislocations in the non-basal planes decreases up to the value necessary for twinning and therefore deformation at temperatures above 200 °C continues via this non-basal dislocation mode.

![Schematic illustration of misorientation associated with an extension twin.](image)

**Figure 4.** Schematic illustration of misorientation associated with an extension twin.

TEM micrographs given in figure 5 show the substructure of the composite with Gr nanoparticles after deformation at (a) room temperature, and (b) 300 °C. In both cases nanoparticles situated in the grain boundaries are clearly visible. Only a few particles were found inside of the grains. This situation is likely to result from the layered structure of the reinforcement. The sliding layers of the nanoparticles were deformed with the grain boundaries and surrounded by the magnesium grains. Owing to similar structure of hBN particles we may consider a similar behaviour also in the BN nanocomposite. After deformation at room temperature the dislocation density is low. In comparison the dislocation density is higher after deformation at 300 °C (see figure 5b).

![TEM micrographs of UFG-Mg+3nGr taken after deformation at RT (a) and 300 °C (b).](image)

**Figure 5.** TEM micrographs of UFG-Mg+3nGr taken after deformation at RT (a) and 300 °C (b).
From figure 1 and 2 it follows that the deformation stresses at 100 and 200 °C are lower for the composite containing Gr nanoparticles although the particle content and preparation technique are the same. Furthermore, the Gr nanocomposite has a smaller grain size in comparison with the BN nanocomposite. Two factors may account for such behaviour:

- The mean grain size of the UFG+3nGr specimens used was estimated to be about 200 nm, compared to the UFGMg+3nBN samples where a value of 600 nm was found. It is possible to consider that for such small grain sizes a negative deviation from the Hall-Petch relationship may be found.
- The bonding between the Gr particles and the Mg matrix is weaker than that for BN nanoparticles. In particular, it is known that Mg does not form carbides and therefore the binding between the matrix and Gr particles is expected to be weak.

These observations are further illuminated by the data in figure 6 showing the amplitude dependence of the internal friction characterised with the logarithmical decrement. The amplitude dependence of the decrement can be divided into two regions. For small amplitudes the decrement does not depend on the amplitude, whereas in the higher amplitudes region the decrement rapidly increases with increasing strain amplitude. While the decrement in the amplitude-independent region is influenced by various mechanisms (including dislocations, grain boundaries, and thermoelastic effects) the amplitude dependent component of the decrement is only due to the presence of dislocations in a material. The amplitude dependency of the decrement, seen in figure 6, shows the influence of grain boundary sliding on the internal friction. The lower decrement values were observed for microcrystalline Mg (μMg) comparing with values measured for ultra fine-grained Mg (UFG-Mg) with the grain size ~ 150 nm. A higher density of grain boundaries increases the decrement due to grain boundary sliding. In the case for the Gr nanocomposite the decrement is very high – in the order 10^{-2}. These high values of the decrement are due to a high contribution of grain boundary sliding as a consequence of the weak bonding between the Mg and Gr nanoparticles. Such behaviour also influences the mechanical properties. Note that all materials were prepared with the same technique – hot extrusion.

The temperature dependence of the Young’s (E) modulus is given in figure 7 for both the BN nanocomposite and pure Mg (prepared also by hot extrusion). It can be seen that the relatively small nanoparticle content significantly increased the modulus. A more quantitative comparison, for example by application of the rule of mixtures, is somewhat problematic in this case because we do not know the influence of texture on the modulus values. The high anisotropy of Mg and especially hBN, together with the sample texture, complicate, therefore, any calculations. We can only conclude that the
nanocomposite modulus rapidly decreases with increasing temperature. At temperatures higher than 325 °C values of the E-modulus in Mg and UFG-Mh+3nBN are practically the same.

The temperature dependence of the thermal expansion coefficient (CTE) estimated for UFG-Mg+3nBN is shown in figure 8a, together with the variation of the CTE for microcrystalline Mg (μMg) also prepared by hot extrusion. The presence of nanoparticles results in a slight decrease in the CTE. For comparison the dependence for polycrystalline Mg (pk Mg) is also introduced. The different course of the temperature dependence estimated for pk Mg and μMg may be explained by the existence of texture in the extruded μMg. The CTE of Mg single crystals exhibit significant anisotropy, with a value in the a direction for CTE(a) = 7.045 x 10^{-6} K^{-1}, and a much higher value in the c direction of CTE(c) = 11.758 x 10^{-6} K^{-1} [16]. Both μMg and UFG-Mg+3nBN exhibit a basal texture with preferential orientation in the long sample axis in which the CTE in the one dimensional approximation is measured.

Pre-deformation in compression results in substantial increase in the CTE at lower temperatures, with less of an effect at higher temperatures, as demonstrated in figure 8b. As it was mentioned above, the compressive plastic deformation of textured magnesium materials is accompanied by the mechanical twinning. As a result parts of grains are reoriented so that the c-axis of the hexagonal magnesium lattice is reoriented nearly parallel with the sample axis. The situation is schematically depicted in figure 8b. Because the CTE is higher in the c-axis direction, reorientation of grains due to twinning increased the sample thermal expansion. Calculated thermal expansion coefficients using rule of mixture (RoM) are slightly higher than the measured values (figure 8a).

![Graph 1](image1)

**Figure 8.** (a) Temperature dependence of CTE for the as-extruded UFG-Mg+3nBN sample, as well as for microcrystalline magnesium (μMg) and coarse grain polycrystalline magnesium (pk Mg); (b) effect of pre-straining in compression (0.5%) on the CTE.

4. **Conclusions**

Magnesium based nanocomposites were successfully prepared by a powder metallurgical route using mixing, followed by milling and then hot extrusion. The reinforcing nanoparticles of either graphite or hexagonal boron nitride exhibit a similar layered structure. Compression tests were performed at elevated temperatures for both nanocomposites, and the temperature dependency of the Young’s modulus and of the thermal expansion coefficient were measured in the composite containing BN nanoparticles. Based on the experimental observations the following conclusions can be made:

- The compressive stress-strain curves of both materials exhibit a similar shape.
- In the low temperature regime the reinforcing effect of BN nanoparticles is much higher in comparison with that for Gr nanoparticles.
- Nanocomposites containing Gr particles are more stable that those containing BN at temperatures higher than 200 °C.
- Weak bonding between Gr nanoparticles and Mg matrix contribute to high damping due to grain
boundary sliding.
- Addition of BN nanoparticles to Mg results in an increased Young's modulus.
- The thermal expansion coefficient of UFG-Mg+3nBN is strongly texture dependent.

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