Magnesium (Mg) nanocomposites reinforced with rare earth element nanoparticles: nanoindentation-driven response

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ABSTRACT
Magnesium (Mg), as the lightest metallic material, is 33% lighter than aluminum which makes it, potentially, a great replacement for aluminum and its alloys. However, Mg in pure and alloyed conditions is brittle at ambient temperature which largely limits their applications. One key solution to enhance the strength and ductility of Mg and its alloys is to embed thermally-stable nano-size reinforcements within the Mg matrix to produce so-called "Mg nanocomposites". The Mg nanocomposites are considering revolutionizing energy-saving lightweight materials of the future with enhanced strength and ductility properties. Mg nanocomposites are, however, at the initial degrees of improvement and consequently, systematic research is required to set up microstructure/property relationships at distinct potential conditions (i.e. temperatures and strain rates). In the present study, a nanoindentation testing approach is adopted to assess ambient-temperature small scale mechanical properties of a group of Mg nanocomposites reinforced with rare-earth element nanoparticles (NPs), i.e. Sm2O3. This paper tried to assess various nanoindentation-driven properties of the Mg-Sm2O3 nanocomposites and compare them with the pure Mg as the baseline.

1. Introduction
Lightweight metal matrix nanocomposites have gained the good-sized attention of researchers in the latest years thinking about as novel substances that could push the boundaries of metals [1, 2]. The metal matrix nanocomposites, with proper ductility and durability along with excessive strength and modulus, could be considered as plausible materials for various industrial applications [3, 4]. Magnesium (Mg) is the lightest metallic material. However, predominant drawbacks of Mg and its alloys including low ductility, low toughness, and terrible corrosion resistance restricted their applications for various applications. One strategy to address these obstacles and enhance the usage of Mg and its alloy is to embed nano-sized reinforcements within the Mg matrix to produce Mg-matrix nanocomposites. These composites may provide a...
special combination of great strength/stiffness, ductility, and increased corrosion resistance along with ideal elevated temperature performance.

Among various metallic and ceramic oxide nanoparticles, rare-earth (RE) oxide nanoparticles have supplied promising effects in refining grain measurement and decreasing the segregation of solute impurities at grain boundaries [5]. Along with nanocomposite of magnesium and rare-earth elements, some nanocomposite of magnesium and oxides of rare-earth have been chosen to improve the strength of the magnesium matrix due to their excellent performances, such as nano-Y2O3 containing magnesium nanocomposites [6, 7] and samarium oxide (Sm2O3) magnesium nanocomposite [8, 9]. Of all the oxides of rare-earth, samarium oxide (Sm2O3) is an attractive rare-earth oxide reinforcement due to its special aggregate of variable valence, excessive thermal stability (melting temperature of 2335°C), superior electronic and optical properties, and high elastic modulus (183 GPa [10]). Kujur et al. [10] studied ignition, compression and damping houses of Mg reinforced with Sm2O3 nanoparticles. They located about 47% reduction in grain size upon addition of Sm2O3 nanoparticles in the Mg matrix compared to pure Mg with resulted in 37% extend in hardness and 53% make bigger in ultimate compressive strength in Mg-1.0 vol% Sm2O3.

Nanoindentation is considered an approach of desire to investigate the mechanical behavior of small volumes, especially to measure the strain rate sensitivity exponent [11–15]. This paper objective at assessing small-scale properties and strain rate sensitivity of pure Mg, Mg-0.5 vol% Sm2O3, Mg-1.0 vol% Sm2O3, and Mg-1.5 vol% Sm2O3 nanocomposites at ambient temperature using a depth-sensing nanoindentation approach.

2. Experiments

Based on the applicable experiences, three special compositions of Mg-0.5 vol% Sm2O3, Mg-1.0 vol% Sm2O3, and Mg-1.5 vol% Sm2O3 nanocomposite rods were synthesized using a powder metallurgy technique, followed by microwave sintering, and hot extrusion [10]. Cylindrical rods, 8-mm in diameter, of the Mg-Sm2O3 nanocomposites and pure Mg were synthesized with the fractions decided above by way of powder metallurgy strategy based on microwave sintering. Hot extrusion accompanied as described in a current paper by way of Kujur et al. [10] with the extrusion ratio of 20 to 1.

The samples were first polished through routine metallography procedure. To study the microstructure of the polished materials, samples were etched using a solution containing 100 ml ethanol, 2.5 g picric acid, 25 ml acetic acid and 25 ml distilled water. A metallurgical optical microscope (model MM500T) and a QUANTA FEG 650 Scanning Electron Microscope (SEM) was used for the microstructural characterizations.

A finely calibrated instrumented nanoindentation device (Hysitron TI Premier TribolIndenter) machine used to be used consisting of a diamond Berkovich indenter with a tip radius of 50 nm. The calibration was once carried out by means of doing one hundred indents from 10 mN to 100 mN on a reference fused quartz specimen. The peak load was set to 10 mN and three different loading rates of 0.05, 0.5, and 5 mN/s were used for each sample.

![SEM micrograph of Sm2O3 nanoparticles distributed with the Mg matrix (Mg-1.0 Sm2O3 nanocomposite).](image_url)
To assure a degree of accuracy of the data, all the indentations were performed along the extrusion direction (ED); To assure reproducibility of the data and to get standard deviations for hardness, 3 to 5 tests were performed at each condition.

3. Results and discussion

3.1. Microstructure

Figure 1 indicates the SEM micrograph of the Sm$_2$O$_3$ nanoparticles in the Mg-1.0 vol% Sm$_2$O$_3$ nanocomposite. It shows that dispersed Sm$_2$O$_3$ nanoparticles in the Mg matrix pinned the recrystallized grain boundaries, which additionally confirms the uniform dispersion of nanoparticles. As the quantity fraction of the nanoparticles varies, two possibilities will come up: (i) inter-particle spacing varies, and (ii) the grain size varies.

Figure 2 provided the micrographs of the pure Mg and the Mg-1.0 vol% Sm$_2$O$_3$ nanocomposite. Severely deformed grains and grain boundaries, brought about by using high extrusion ration, are observed. When the volume of the Mg-Sm$_2$O$_3$ nanocomposite. It shows that dispersed Sm$_2$O$_3$ nanoparticles in the Mg matrix pinned the recrystallized grain boundaries, which additionally confirms the uniform dispersion of nanoparticles. As the quantity fraction of the nanoparticles varies, two possibilities will come up; (i) inter-particle spacing varies, and (ii) the grain size varies.

Figure 2 provided the micrographs of the pure Mg and the Mg-1.0 vol% Sm$_2$O$_3$ nanocomposite. Severely deformed grains and grain boundaries, brought about by using high extrusion ration, are observed. When the volume of the Mg-Sm$_2$O$_3$
nanocomposites elevated from 0 to 0.5% and then to 1.0%, grain measurement and interparticle spacing decreased. However, when the volume fraction of the Sm$_2$O$_3$ nanoparticles accelerated from 1.0% to 1.5% a contrary fashion occurred. That is, 1.0 vol.% Sm$_2$O$_3$ nanocomposite is a key content to decide which volume fraction is the optimum value. This will be evaluated more in detail in the coming sections.

3.2. Nanoindentation response

Figure 3 shows the loading portion of the load/displacement plots for one of the nanocomposites studied in this paper (Mg-1.0% Sm$_2$O$_3$ nanocomposite). As seen, at a constant depth of say 500 nm, with an increase in the loading rate, the indentation load increases. This is an indication of rate sensitivity showing that the studied structures are rate-sensitive at room temperature (this will be discussed later in this paper). The $P$–$h$ curve from the loading process can be described by Kick’s Law, $P = Ch^2$, where $C$ is the loading curve curvature [16].

Pop-in events during the loading in the nanoindentation of the studied materials are obvious as shown in Figure 4. Pop-ins are considered a sudden increase in depth under a constant load and this is attributed to a sudden movement of dislocation generated from Frank-Read sources. For the slow loading rate, since the rate of data acquisition is slow, the pop-in event is clearly seen around 25 nm depth. However, with an increase in the loading rate, the pop-in event is less distinguishable due to many data recorded per second. For instance, in the case of a loading rate of 5 mN/s, the event is observed around 250 nm depth while in the slowest leading rate of 0.05 mN/s, it is not clear where this phenomenon occurs (though it is there).

Jian et al. [17] and Lorenz et al. [18] assessed the look of pop-ins in the nanoindentation and mentioned their existence related to the homogeneous dislocation nucleation (generation) mechanisms. Recent research [19–21] confirmed that the “pop-in” behavior in load-displacement curves of coarse-grained pure Mg and AZ31 used to be related to $<1012>$ twins on the surface. The “pop-in” occasions in the load-displacement curves of as-received Mg suggest deformation twinning in these materials. Ghasemi et al. [19] assessed microstructure and nanoindentation response of Mg-SiC nanocomposites and in contrast the effects with pure Mg. They said the pop-in effect in the loading curves of the as-received coarse-grained pure Mg and not always in the nanocomposites with nano-crystalline and/or ultra-fine grain size. However, we do not claim an ultra-fine grain shape in our fabricated Mg-Sm$_2$O$_3$ nanocomposites. Therefore, the “pop-in” consequences in the cloth studied may be a manifestation of the homogeneous nucleation for glissile dislocation loops of the course-grained nanocomposite.

It is worth mentioning that the loading rates of 0.05, 0.5, and 5 mN/s correspond with 200, 20, and 2 s, respectively, the time required to reach the peak load (see Figure 5). The slopes of the plots in Figure 5 provides the indentation strain rate and as is seen the strain rate is not constant through the test (very high at the beginning and then a diminishing trend).

Indentation hardness ($H_{ind}$) can be determined from the load/depth plots employing the following equation:

![Figure 3. The load-displacement plots of the Mg-1.0% Sm$_2$O$_3$ nanocomposites at three tested loading rates.](image)
Figure 4. Evidences of the pop-in effect in the Mg-1.0% Sm₂O₃ nanocomposite.
\[ H = \frac{P}{A(h_c)} \]  
\[ A_c = 24.56h_c^2 \]  
\[ h_c = h_{\text{max}} - \varepsilon \frac{P_{\text{max}}}{S} \]

where \( \varepsilon \) is a constant with a value of 0.75 and \( S \) is the contact stiffness at the initial unloading (the slope of the unloading portion of the load/displacement plot). Table 1 provide the indentation hardness (in GPa) at the employed loading rates for the tested materials including the pure Mg and the Mg nanocomposites. As you see with an increase in the loading rate indentation hardness increase where the highest hardness values belong to the Mg-1.0 Sm\(_2\)O\(_3\) nanocomposite material. This is interesting as the indentation hardness does not necessarily enhance with the increase in the volume fraction of the Sm\(_2\)O\(_3\). This validates the deduced modified Hall-Petch equation which indicates that there exists an optimal volume fraction for the optimum mechanical properties. If the extent fraction exceeds a positive level, they finally agglomerate and form clusters of particles that cannot anymore be considered as nanoparticles (rather microparticles). During loading, these so-called microparticles would either crack or detach from the matrix ensuing in loss of strength.

This observation that the indentation hardness is a function of the indentation loading rate confirms that the studied materials are rate-sensitive at room temperature. To better assess this observation, natural logarithm (\( \ln \)) of indentation hardness (\( H_{\text{ind}} \)) versus \( \ln \) of indentation strain rate (i.e. double logarithmic curve of hardness versus indentation strain rate), for various materials tested in this study, is plotted in Figure 6. The corresponding linear equations are provided in the same figure. High correlation coefficients (\( R > 0.90 \)), implying that these functions can properly measure the dependence of nanoindentation stress on the strain rate. Error bars on the data reflect the standard deviation calculated for hardness from the multiple indentations for each sample. The strain rate sensitivities (\( m \)-value) are measured as 0.0127, 0.0164, 0.0329, and 0.0192 for pure Mg, Mg-0.5 Sm\(_2\)O\(_3\), Mg-1.0 Sm\(_2\)O\(_3\), and Mg-1.5 Sm\(_2\)O\(_3\), respectively.

Reduced elastic modulus (\( E_r \)) is an indication of the elastic deformation that occurs in each specimen and indenter tip. In the nanoindentation \( P-h \) curves, \( E_r \) can be calculated from the preliminary slope of the unloading curve the usage of the following correlation:

\[ E_r = \frac{\sqrt{\pi} S}{2 A_c} \]

where, \( A_c \) and \( S \) are the contact area and stiffness, respectively.

Young’s modulus of the specimen, \( E_s \), can be calculated from the reduced modulus \( E_r \) using the relation [22]:

| Material          | 0.05 mN/s | 0.5 mN/s | 5 mN/s | 0.05 mN/s | 0.5 mN/s | 5 mN/s |
|-------------------|-----------|----------|--------|-----------|----------|--------|
| Mg-1.0 Sm\(_2\)O\(_3\) | 0.65 GPa  | 0.55 GPa | 0.51 GPa | 0.66 GPa  | 0.57 GPa | 0.52 GPa |
| Mg-1.5 Sm\(_2\)O\(_3\) | 0.71 GPa  | 0.64 GPa | 0.55 GPa | 0.52 GPa  | 0.52 GPa | 0.53 GPa |
| Pure Mg           | 0.51 GPa  | 0.52 GPa | 0.53 GPa | 0.51 GPa  | 0.52 GPa | 0.53 GPa |

Table 1. variations in hardness versus loading rate versus material.
\[ E_s = \frac{E_i E_s (1 - v_s^2)}{E_i - E_s (1 - v_s^2)} \]  

(5)

where \( v_s \) is the specimen Poisson ratio (0.33), \( v_i \) is the Poisson ratio of indenter (0.07 for the diamond) and \( E_i \) is Young’s modulus of the indenter, 1140 GPa [23].

Figure 7 shows the reduced modulus as a function of volume fraction of \( \text{Sm}_2\text{O}_3 \) nanoparticles in the Mg matrix at different indentation loading rates. With the increase in the volume fraction of \( \text{Sm}_2\text{O}_3 \) nanoparticles, Young’s modulus varied. Compared to pure Mg (0 vol.% \( \text{Sm}_2\text{O}_3 \)), addition of 1.0 vol.% \( \text{Sm}_2\text{O}_3 \) nanoparticles, resulted in Young’s modulus

![Figure 6. Indentation hardness versus indentation loading rate for different materials studied in this paper.](image1)

![Figure 7. Reduced modulus versus volume fraction of \( \text{Sm}_2\text{O}_3 \) nanoparticles in the Mg matrix.](image2)
increase by 18%, 19%, and 21% for 0.05 mN/s, 0.5 mN/s, and 5 mN/s load rates, respectively. An increase in the volume fraction of Sm$_2$O$_3$ nanoparticles in the Mg matrix increases its stiffness. Also, for a constant vol. % of Sm$_2$O$_3$ (say 1%), an increase in loading rate resulted in modulus increase. This may be attributed to enhanced work hardening which is proportional to the loading rate (larger at a higher loading rate). Sm$_2$O$_3$ nanoparticles have higher elastic modulus (~183 GPa [10]) compared to the Mg matrix, which leads to an increase in the overall elastic modulus of the nanocomposites as the Sm$_2$O$_3$ volume fraction increases.

The indentation stress for all the materials decreases with an increase in indentation depth. Some researchers attributed this to the indentation size effect (ISE) of dislocation-starved plasticity (DSP) [24] or strain-gradient plasticity (SGP), induced by geometrically necessary dislocations (GNDs) [25]. In the case of nanoparticle, along with the DSP and the SGP, one needs to consider the contribution of the nanoparticles as well. This is yet to be considered how the nanoparticles contribute to the ISE. Based on the Nix-Gao model [25] there is a linear relationship between the square of indentation hardness and the inverse of the indentation depth:

\[
H_{\text{ind}}^2 = H_0^2 \left(1 + \frac{h^*}{h}\right)
\]

where \( h \) is contact depth and \( h^* \) is an internal indentation length scale, which can describe the degree of the ISE. \( H_0 \) is the hardness at large depth where statistically stored dislocations (SSDs) are the contributing ones. Based on the Nix-Gao model both GNDs and SSDs contribute to the hardness of materials where GNDs are controlling dislocations at shallow depth and the SSDs are the controlling dislocations in large depth.

Figure 8 shows the \( H^2 \) versus \( 1/h \) for the tested materials at a constant load rate of 5 mN/s (as a representative). As expected, with the increase of \( 1/h \), the value of the square of hardness increases linearly. According to the results of the linear fitting, values of \( H_0 \) and \( h^* \).

**Conclusions**

Small-scale mechanical properties of Mg-Sm$_2$O$_3$ nanocomposites, with three different volume fractions of Sm$_2$O$_3$ nanoparticles, were investigated and compared with pure Mg. The following conclusions were drawn:

1. The 1.0% volume fraction of Sm$_2$O$_3$ is the optimal content that provides the highest strength.
2. The peak hardness is observed in the Mg-1.0 Sm$_2$O$_3$ and the indentation hardness increases with the increase in the loading rate.
3. The GNDs, the SSDs, and the nanoparticles contribute to the observed ISE; the impact of the nanoparticles on the ISE needs to be further studied.
Disclosure statement

No potential conflict of interest was reported by the authors.

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