**SUPPLEMENTARY MATERIAL**

**Strengthening mechanisms contributing to the tensile yield strengths of Mg-SiO2 nanocomposites**

Orowan strengthening is a result of the resistance offered by ultrafine hard particulates to the dislocation movement [1, 2]. Orowan strengthening explains the strengthening effect as a factor of particle dimensions and the experimentally achieved interparticulate spacing between the SiO2 nanoparticulates. The Orowan loop mechanism forms dislocation loops around the nanoparticulates leading to work hardening effects and contributes to strengthening of MMNCs [2]. Orowan strengthening () is given by the following Equation (1) [3] :

|  |  |
| --- | --- |
|  | (1) |

where, G is the shear modulus of magnesium (17.3 GPa) [4] , b is the burgers vector of magnesium (3.21 × 10−10 m) [5] and r is the average radius of nanoparticulates, respectively. The interparticulate spacing () between the magnesium matrix and nanoparticulates is given by the Equation (2) [6] :

(2)

where, dp and Vp are the average diameter and volume fraction of nanoparticulates.

The activation of Orowan strengthening mainly depends on the interparticulate spacing () which can be achieved through uniform dispersion of nanoparticulates within the matrix. In order to achieve an uniform distribution of nanoparticulates within the Mg matrix, various factors such as the particle size of the nanoparticulates, volume fraction of the nanoparticulates within the matrix and synthesis methodology enabling uniform distribution of nanoparticulates are of prime importance [7]. The theoretical interparticulate spacing () is calculated by the Equation (2), where the average diameter of the nanoparticulate is as mentioned by the supplier, dp (~15 nm) and Vp (0.5, 1 and 2 vol. %) is the volume fraction of nanoparticulates reinforced within the magnesium matrix. This λTheoretical value is then substituted in Equation (1) to calculate the theoretical Orowan strengthening contribution in MPa. The experimental measurements of the interparticulate spacing as shown in Fig. 2 in the nanocomposites (λobserved) using FESEM are used directly in to Equation (1) to calculate the experimental orowan strengthening contribution in MPa. Theoretically predicted and experimentally calculated interparticulate spacing (λ) values of SiO2 nanoparticulates within the Mg matrix are shown in Table SI. For example, the theoretical and experimental λ values for a size range of ~15 nm in Mg 2 vol. % SiO2 nanocomposites is ~28 nm and ~1142 nm, respectively and exhibit a theoretical and experimental of ~78 MPa and ~2 MPa, respectively. The experimentally determined is insufficient to activate the Orowan strengthening in Mg-SiO2 nanocomposites. The minimal contribution of Orowan strengthening in the Mg-SiO2 nanocomposites may be attributed to the ineffectiveness of the adopted synthesis methodology to uniformly disperse the nanoparticulates within the Mg matrix. From the available literature, it can be observed that even though Mg-based nanocomposites have reported enhanced properties owing to effective distribution of nanoparticulates within the matrix contributing to Orowan strengthening, an in-depth investigation of the interparticulate spacing and effectiveness of the synthesis technique towards uniform dispersion of nanoparticulates must be carried out. Further, for the adopted synthesis technique, the dispersion of nanoparticulates mainly depends on the blending speed and time, compaction and sintering parameters, extrusion ratio and the difference in densities between the nanoparticulates and the matrix.

The addition of SiO2 nanoparticulates leads to a marginal decrease in the grain size (Table I) of pure Mg. Hall-Petch strengthening mechanism is used to understand and predict the effect of grain size on the strength of the material [8]. The reduction in grain size will enhance the strength properties of the material. Equation (3) shows the relationship between the grain size and the strength of the material [8]:

|  |  |
| --- | --- |
|  | (3) |

Where K is the Hall-Petch coefficient of Mg (280 MPa·μm1/2) and D is the average grain size (μm) of the Mg-SiO2 nanocomposites. It has been previously reported in the literature that the particle size of nanoparticulates, volume fraction of nanoparticulates within the matrix and fabrication method used are significant factors to be considered to achieve a reduction in the grain size of MMNCs [2, 9]. The contribution of Hall-Petch strengthening mechanism on the 0.2 % TYS of the Mg-SiO2 nanocomposites can be calculated by Equation (3). Mg (0.5, 1 and 2) vol. % SiO2 nanocomposites exhibited of ~51 MPa, ~54 MPa and ~58 MPa, respectively. The Hall-Petch strengthening contribution is observed to only marginally increase with the increasing amount of SiO2 nanoparticulates which can be attributed to the limited decrease in the grain size of pure Mg with the addition of SiO2 nanoparticulates (see Table I).

The strengthening due to the mismatch of coefficient of thermal expansion (CTE) values of magnesium matrix and reinforcement particulates leading to the increase in the dislocation density of the composite is known as Forest strengthening. Forest strengthening due to the CTE mismatch can be given by the Equation (4) and (5) [7]:

|  |  |
| --- | --- |
|  | (4) |
|  | (5) |

Where A is, a constant characterizing the transparency of dislocation forest for basal-basal interaction in Mg (0.2) [5], M is the mean orientation factor for Mg (6.5) [5], is the dislocation density, ∆T is the temperature excursion which is chosen to be 250 K (for all the nanocomposites) assuming that the dislocation begins at 550 K corresponding to a stress-free homologous temperature of 0.6 [5] and ∆α is the difference in the CTE values between the reinforcement particulates and magnesium matrix. Theoretically, the presence of ultrafine nanoparticulates must increase the forest strengthening contribution ( ) value. However, Vogt et al. [10] has experimentally concluded that the forest strengthening contributions will be low for particulate size less than 80 nm due to limitations of synthesis techniques to disperse ultrafine nanoparticulates. Further, Forest strengthening can only be realized with the addition of higher volume nanoparticulates (> 10 vol. %) [11].

Mismatch in the elastic modulus value of the matrix and reinforcement particulates leading to the formations of dislocations under application of external load is known as Taylor strengthening. The strengthening contributions are given by Equations (6) and (7) [8] :

|  |  |
| --- | --- |
|  | (6) |
|  | (7) |

where is the density of dislocations due to modulus mismatch and α is a constant (0.5). Theoretically, higher the volume percent addition of SiO2 nanoparticulates, greater is the strengthening contribution. It has been observed that the dislocations produced by work hardening effect during extrusion are accumulated mostly in the coarse grain regions than the finer grain regions making the density of dislocations insignificant. Further, the contribution of Taylor strengthening as compared to other strengthening mechanisms may be considered negligible in case of magnesium matrix nanocomposites [12].

The presence of strong interfacial bonding between magnesium matrix and SiO2 nanoparticulates may help in the effective load transfer from softer magnesium matrix to harder SiO2 nanoparticulates. The strengthening contribution due load transfer is given by the Equation (8) [13]:

|  |  |
| --- | --- |
|  | (8) |

Where is the 0.2 % TYS of pure magnesium. The addition of (0.5, 1 and 2) vol. % SiO2 nanoparticulates in magnesium matrix exhibited a load transfer contribution () of ~0.21 MPa, ~0.43 MPa and ~0.9 MPa respectively. Hence, for modeling of low volume fraction SiO2 nanoparticulates in magnesium matrix, the load transfer contributions are considered to be insignificant [7].

The strengthening contribution of mismatch in CTE values (), mismatch in modulus values () and load bearing effect () is considered to be insignificant for the current study for the addition of low volume SiO2 nanoparticulates of size range ~15 nm within the Mg matrix [10, 12]. In addition to that, the contribution to Orowan strengthening when calculated for the observed λ values is almost negligible. Hence, Hall-Petch mechanism is the major strengthening mechanism contributing towards the marginal increase in the 0.2% TYS of Mg-SiO2 nanocomposites.

For theoretical prediction of the tensile yield strength (TYS), modified Clyne model was utilized. This model was developed by Sanaty-Zadeh [8] in which the square root of sum of the squares of contributions of each strengthening mechanisms is calculated and added to the 0.2 % TYS of pure Mg ().

(9)

In the current study, insignificant contributions due to , and and non-activation of Orowan strengthening and significant contribution of the Hall-Petch mechanism will reduce the Equation (9) to the following Equation (10). The theoretical 0.2 % TYS values of the Mg-SiO2 nanocomposites are calculated utilizing the Hall-Petch model (Equation (10)) and compared with the experimental TYS values in Table SII.

(10)

Theoretical 0.2 % TYS values were still higher than experimental 0.2 % TYS values suggesting that the effects of porosity and textural changes must be taken in account to accurately predict the strength values.

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TABLE SII. Contribution of different strengthening mechanisms and predicted values of tensile yield strength of Mg-SiO2 nanocomposites

TABLE SI.Effect of interparticulate spacing between the SiO2 nanoparticulates in the Mg matrix on the Orowan Strengthening contribution

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Sl. No | Material  (vol. %) | Interparticulate Spacing (nm) | | σOrowan  (MPa) | |
| λTheoretical | λobserved | Theoretical | Experimental |
| 1 | Mg0.5SiO2 | 54 | 2000 | 41 | 1.13 |
| 2 | Mg1SiO2 | 40 | 1460 | 56 | 1.62 |
| 3 | Mg2SiO2 | 28 | 1142 | 78 | 1.98 |

TABLE SII. Contribution of different strengthening mechanisms and predicted values of tensile yield strength of Mg-SiO2 nanocomposites

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Sl. No | Material  (vol. %) | 0.2% TYS  Experimental  (MPa) | σOrowan\*    (MPa) | σHall-Petch  (MPa) | 0.2% TYS  Theoretical  (MPa) |
| 1 | Mg0.5SiO2 | 85 | 1.13 | 51 | 138 |
| 2 | Mg1SiO2 | 94 | 1.62 | 54 | 141 |
| 3 | Mg2SiO2 | 114 | 1.98 | 58 | 145 |

\* Experimentally calculated Orowan strengthening contribution