Influence of silica nanospheres on corrosion behavior of magnesium matrix syntactic foam

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Abstract. Over the years, the development of Magnesium alloys as biodegradable implants has seen significant advancements. Magnesium based materials tend to provide numerous advantages in the field of biomedical implants over existing materials such as titanium or stainless steel. The present research focuses on corrosive behavior of Magnesium reinforced with different volume percentages of Hollow Silica Nano Spheres (HSNS). These behaviors were tested in two different simulated body fluids (SBF) namely, Hank’s Buffered Saline Solution (HBSS) and Phosphate Buffered Solution (PBS). This corrosion study was done using the method of electrochemical polarization with a three-electrode configuration. Comparative studies were established by testing pure Mg which provided critical information on the effects of the reinforcing material. The HSNS reinforced Mg displayed desirable characteristics after corrosion experiments; increased corrosion resistance was witnessed with higher volume percentage of HSNS.

1. Introduction
Magnesium (Mg) has proven to be a viable material in the field of biomedical implants due to its mechanical properties which bear close resemblance to that of a human bone [1]. Moreover, these properties of Mg based materials allow for great results of machinability, thermal stability, damping characteristics, and ability to resist electromagnetic radiation [2]. Even with all these capabilities Mg has a major drawback which is the sole reason for it not being accepted globally as the standard material for temporary implants, which is its low corrosion resistance. This very reason limits the potential of Mg in the medical industry. In recent years, advancements have been made to synthesize alloys of Mg in hopes of obtaining desirable corrosion resistance with little success. From literature it is imperative that additional efforts need to be put into enhancing the properties of Mg based materials. Mg syntactic foam based composites have proven to push boundaries of specific properties to the potential limit [3] which make them the focus of this study.

Syntactic foams are closed cell materials which incorporate hollow spheres/particles into a metal matrix. Rather than having air or gas to create voids which give the material high porosity, hollow
spheres are used to provide a reinforcement structure to the metal matrix as well as enhance specific properties of the composite in general [4]. The main motive of these hollow sphere reinforcements was to make the material light weight as well as have a cushion between the metal matrix to allow for better compressibility. Moreover, successful synthesis of these materials with proven enhancement in mechanical properties over pure Mg has led to the question whether this composition has affected the rate of corrosion in a positive manner as well.

Previously conducted studies have shown that the rate of corrosion for such materials tends to be higher. The reason attributed to the increase in corrosion rate are the interfaces that are left void between the metal matrix and the reinforcements. Moreover, due to the difference in material, a larger potential difference is created between the metal matrix and reinforcement [5,6]. On the other hand, some studies have also suggested improvement of corrosion rate due to presence of the reinforcement material. This behavior has been credited to the reduced exposure of metal to the corrosive environment; with a mixture of reinforcement material as well as metals, there is less surface area from the metal that reacts to the corrosive environment which helps reduce its rate of corrosion [7]. For this research, a comprehensive study over corrosion rate of Mg reinforced with Silicon dioxide (SiO2) HSNS is established. The electrolytes used are two Simulated Body Fluids (SBF) and the results are then compared to pure Mg which is manufactured using the same technique.

2. Experimental
Disintegrated Melt Deposition (DMD) is a very unique and inexpensive method of manufacturing which brings about the advantages of both spray processing and conventional casting. The Mg matrix reinforced with HSNS was synthesized using DMD method. This method utilizes high superheated temperatures and low impacting velocities of gas jets to manufacture bulk composites. Synthesis of nano-spheres reinforced magnesium composites using DMD method requires heating the magnesium chips/turnings along with the reinforcement powder to be placed in a multi-layered arrangement inside a graphite container with superheated conditions of greater than 650°C under inert gas atmosphere, usually argon, in a crucible made of graphite with a resistance heating furnace. The graphite crucible is installed with an arrangement for bottom pouring [5]. Once the molten slurry reaches temperatures of above 650°C, the stirring process is initiated for 5 minutes at a RPM of 450. This is done using a twin blade, pitch angle 45°, impeller that accelerates the merging of the HSNS into the metal matrix as well as ensuring even distribution and temperature across it. To avoid any contamination of the blade, it is coated with Zirtex 25 (86% ZrO2, 8.8% Y2O3, 3.6% SiO2, 1.2% K2O and Na2O, and 0.3% trace inorganic). Once the melt is evenly mixed, it flows down through an orifice of 10 mm at the bottom of the graphite container. Two argon jets are introduced at normal orientation to the melt which are used disintegrate it before being deposited on a metal substrate [8]. The ingots that results from this procedure were machined down to billets of length 45 mm and diameter 36 mm. Further processing was then done one these billets to get desirable dimensions for testing of mechanical properties. The billets were hot extruded using an extrusion ratio of 20.25:1 which resulted in rods of 8mm diameter [3]. This procedure was carried out for pure Mg, 0.5 vol. % HSNS, 1.0 vol. % HSNS, 1.5 vol. % HSNS, and 2.0 vol. % HSNS.
Electrochemical polarization is a form of accelerated corrosion testing which allows the material’s behavior to be observed in different physiologically relevant simulated environments. The apparatus utilized for this experimentation was a PGSTAT204 as well as a three-electrode configuration where the Reference Electrode (RE) was made of saturated calomel, and the Counter Electrode (CE) was made of Platinum. The material used as Working Electrode (WE) were samples of Mg-HSNS syntactic foam as well as Pure Mg which were ultrasonically degreased with acetone and rinsed with distilled water prior to the electrochemical measurements. The simulated environments were actuals two different SBF’s namely, Phosphate Buffer Solution (PBS, pH 7.4) and Hank’s Buffered Saline Solution (HBSS, pH 7.4). Both solutions comprised of analytical reagent grade chemicals using distilled water. The compositions of the electrolytes are listed in Table 1 [9].

To carry out electrochemical polarization, some parameters needed to be set to obtain proper results. The scan rate was set to 0.000167 mV/s to obtain a smooth polarization curve and OCP determination time was set to 900 seconds to provide ample time for open circuit potential to stabilize. The WE comprised of a copper piece that provided enough depth for the actual sample to be immersed in the electrolyte. Only a small portion of the sample was exposed to the electrolyte while the rest that was in contact with the copper was covered in Teflon to provide maximum electric isolation and ensure no copper came in contact with the electrolyte.

Table 1 Compositions (g/L) of phosphate buffered solution, and hank’s buffered saline solution [9].

| COMPOSITIONS (G/L) | PHOSPHATE BUFFERED SOLUTION (PH 7.4) | HANK’S BUFFERED SALINE SOLUTION (PH 7.4) |
|-------------------|-------------------------------------|-----------------------------------------|
| NACL              | 8.0                                 | 8.0                                     |
| NAHCO₃            | -                                   | 0.35                                    |
| NAH₂PO₄           | 1.15                                | -                                       |
| KCL               | 0.2                                 | 0.4                                     |
| KH₂PO₄            | 0.2                                 | 0.06                                    |
| CACL₂.2H₂O        | -                                   | 0.19                                    |
| MgSO₄.7H₂O        | -                                   | 0.2                                     |
| Na₂HPO₄.7H₂O      | -                                   | 0.09                                    |
| GLUCOSE           | -                                   | 1.0                                     |
3. Results

3.1 Phosphate Buffered Solution

Figure 2 Polarization curves for Mg HSNS SiO₂ and Pure Mg in phosphate buffered solution (PBS).

The results of electrochemical polarization in PBS can be seen in figure 2. The first thing that is noticed in the figure are the smooth polarization curves that are obtained from the experiment. This ensures stability amongst all the samples that were tested for corrosion. Tafel extrapolation of polarization curves is used to determine corrosion current density ($i_{corr}$) and corrosion potential ($E_{corr}$) values. While the curve of Pure Mg displays a higher $E_{corr}$ value than most of the samples, Mg-1.0 % HSNS has a smaller $E_{corr}$ value as well as a significantly smaller $i_{corr}$ value which generally denotes an enhanced corrosion resistance. It is also noticed that most all the other samples of the reinforced syntactic foam have a very similar graph compared to Pure Mg which is why the following table is used to further clarify the results.

Table 2 Corrosion Potential ($E_{corr}$), Corrosion Current Density ($i_{corr}$), Corrosion rate and Polarization resistance of Mg HSNS SiO₂ and Pure Mg in phosphate buffered solution (PBS).

| Composition | $E_{corr}$ (V) | $i_{corr}$ (μA/cm²) | Corrosion Rate (mm/year) | Polarization Resistance (Ω) |
|-------------|----------------|----------------------|--------------------------|-----------------------------|
| Pure Mg     | -1.5471        | 133.21               | 3.0047                   | 41.213                      |
| 0.5% SiO₂   | -1.5514        | 46.032               | 1.0337                   | 24.438                      |
| 1.0% SiO₂   | -1.5634        | 6.1619               | 0.13772                  | 136.39                      |
| 1.5% SiO₂   | -1.5525        | 46.149               | 1.0261                   | 26.367                      |
| 2.0% SiO₂   | -1.5416        | 390.93               | 8.647                    | 20.387                      |

The table above gives a more meaningful insight to the results of polarization. As discussed previously, Mg-1.0 % HSNS has a significantly smaller $i_{corr}$ value when compared to Pure Mg. This translates to a very high polarization resistance, almost 3 times to that of Pure Mg. While the other compositions performed lower than Pure Mg in terms of polarization resistance, their corrosion rate...
was still significantly lower except for Mg-2.0% HSNS which displayed the highest rate of corrosion. These results show enormous potential in the synthesized material that is being tested.

3.2 Hank’s Buffered Saline Solution

The polarization curves from electromechanical polarizations in HBSS can be seen in figure 3. As with the results of PBS experiment, smooth curves can be seen for this experiment as well ensuring stability of the samples. However, the curves seem to show the Pure Mg sample out performing all other samples with lower \(E_{corr}\) and \(i_{corr}\) values being displayed. These graphs may be showing a better performance for Pure Mg however, taking a closer look at the results shows something different. The values in the following table show improved performance of all samples containing reinforcement when compared to Pure Mg.

Table 3 Corrosion Potential (Ecorr), Corrosion Current Density (icorr), Corrosion rate and Polarization resistance of Mg HSNS SiO2 and Pure Mg in hank's buffered saline solution (HBSS).

| Composition | Ecorr (V) | icorr (μA/cm2) | Corrosion Rate (mm/year) | Polarization Resistance (Ω) |
|-------------|----------|----------------|--------------------------|-----------------------------|
| Pure Mg     | -1.502   | 29.21          | 0.65886                  | 265.84                      |
| 0.5% SiO2   | -1.4882  | 19.185         | 0.4308                   | 130.07                      |
| 1.0% SiO2   | -1.50747 | 13.608         | 0.30413                  | 198.48                      |
| 1.5% SiO2   | -1.5427  | 6.6374         | 0.14759                  | 238.75                      |
| 2.0% SiO2   | -1.5217  | 2.8041         | 0.062024                 | 762.75                      |

The values in table 3 show that Mg-2.0% HSNS has outperformed Pure Mg by a large margin. The corrosion rate has decreased to a tenth of the value of Pure Mg and the polarization resistance has increased three folds. The other samples with reinforcement also showed desirable results with the
corrosion rate decreasing as the vol. % of HSNS increased. These results again verify the fact that addition of reinforcement material has indeed enhanced the performance of the composite.

Initially discussed briefly, existing literature suggests the reason as to why corrosion rate is reduced with the presence of hollow spheres in the metal matrix [7]. The main reason is the reduction of exposed metal matrix to the corrosive environment. Due to presence of hollow spheres, for any given vol. %, magnesium content is bound to decrease compared to pure Mg. Voids within the matrix are filled by hollow spheres which provide enough resistance to corrosion to make noticeable improvement to the corrosion rate. Pure magnesium has been tested for corrosion in many studies. Existing literature shows that pure Mg disperses hydrogen bubbles as soon as it is immersed in the solution due its highly reactive nature. With progression of time, the bubble formation reduces. Deposits of MgO and Mg(OH)\textsubscript{2} are noticeable on the surface which behave like a protective film and slow down the corrosion rate. Through all this, material deformation also takes place where pitting is visible and localized corrosion is identified [10].

4. Conclusion
A few conclusions can be deduced from the electrochemical polarization of Mg matrix reinforced with HSNS:

1. Addition of HSNS reinforcement enhanced corrosion resistance of the material when compared to Pure Mg.
2. Mg-1.5\% HSNS was overall the best composition as it provided consistent results which were better than Pure Mg in both electrolytes.
3. Each solution affected the samples in a separate way. This can generally be constituted to the varying composition of the SBF’s.

The existing studies has shown potential in the newly synthesized Mg reinforced with HSNS. Similar experiments need to be carried out with other common SBF’s such as Artificial Saliva Solution (ASS) and Artificial Blood Plasma Solution (ABPS) to gain further knowledge on the affect of HSNS in corrosion. Surface morphology also needs to be studied to determine the nature of corrosion.
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