Additive manufacturing of immiscible bimetallic composites for biodegradable implants

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INTRODUCTION: Metallic implants are a common occurrence in the fields of medicine and surgery. Depending on the location of the implant, it could be designed to be permanent (like joints) or temporary/resorbable. In some specific cases (like fractures), implants (for example, plates and screws) are used for fixation which take away some (or all) of the load off the bone to promote their healing. However, once the bone is healed, the implant can be detrimental if left affixed. Some of effects could be – infection sites, stress shielding (the bone is still not taking the loads that it normally would, which is its mechanism to maintain strength), debris formation leading to lodging of toxins into the bloodstream. Even more so, in case of pediatric patients, these implanted devices can lead to growth inhibition and are to be removed after fulfilling their intended purpose. Hence, typically fractures require revision surgeries to remove the implanted devices which are a source of unwanted trauma for the patients. To tackle the aforementioned issues with the existing state-of-the-art implants, we propose the usage of biodegradable implants. These implants will also have tunable degradation rate to allow us to match the degradation with bone healing and slowly transfer the complete load onto the healed bone.

METHODS: Biodegradable metals are currently limited to only three – Iron (Fe), Zinc (Zn) and Magnesium (Mg). Among these, Fe has the slowest degradation rate while Mg is the fastest (which is beneficial for short term implants). Zinc has an intermediate degradation rate with unattractive mechanical properties. Fe on the other hand has very good mechanical properties like fatigue life, while Mg has a Young’s modulus close to that of the bone. Hence, we chose the immiscible system of Fe-Mg to have properties that are best of both worlds. Though it isn’t possible to manufacture immiscible compositions via conventional manufacturing routes, the advent of additive manufacturing (AM) has made it possible due to its inherent characteristics. AM has very high cooling rates (10⁶ – 10⁷ K/s). Marangoni convections (that induce natural mixing) and small melt pool dimension in comparison to the part dimensions. Samples of three materials – pure Fe, pure Mg and Fe-Mg were manufactured using Directed Energy Deposition (DED). Pure Fe and pure Mg samples are used as baseline to compare against the degradation of our material system, Fe-Mg. Microstructural analysis of the manufactured samples was done using a Scanning Electron Microscope (SEM) along with Energy Dispersion Spectroscopy (EDS). The presence of both the Fe and Mg phases has been confirmed with the help of X-Ray Diffraction (XRD). Immersion studies were carried out for the samples in a simulated body fluid (SBF) at 37°C to mimic the conditions of a human body. Immersion studies have been carried out with a single surface of the sample exposed (2D) and the entire sample as is (3D). During these immersion studies, periodic readings were taken for pH of the solution and the weight of the samples. Post immersion, the samples were once again analyzed using SEM and EDS.

RESULTS: The SEM micrographs reveal the heterogeneous distribution of Mg across the Fe matrix (Fig 1 (a)). Though, at much smaller length scales we see somewhat of a homogeneous distribution (Fig 1 (b)). XRD corroborates this finding with multiple peaks for both Fe and Mg (Fig 1 (c)). The stochastic nature of the distribution of Mg can be attributed to the Marangoni convections in unison with high cooling rates which kinetically freeze Mg in various locations. The immersion studies were carried out for about 65 days revealed the degradation rates of the various materials – Mg >> Fe-Mg >> Fe (Fig 1 (d)). Here, we noticed the pure magnesium sample fully degrade in about 10 days’ time whereas the pure iron sample saw minimal change in mass over the 65 days. The degradation of pure Mg was much quicker than reported in literature which could be due to printing defects. The designed immiscible bimetallic composite showed an improved degradation in comparison to pure Fe by an extra 11% in the same time span (Fig 1 (f)). Not only did it outperform pure Fe in terms of degradation rate, but it also had a more controlled hydrogen gas evolution which is a known issue with magnesium and magnesium-based implants (Fig 1 (e)). The slower release of hydrogen gas helps the blood filter out excess bases more easily and also prevents the formation of hydrogen warts in the nearby/surrounding tissues.

DISCUSSION: The hypothesis that magnesium regions would act as galvanic cells for the materials’ degradation was confirmed with the help of the 2D and 3D immersion studies. Magnesium being the more electronegative metal gets selectively attacked by the SBF first leaving pits in the iron matrix (Fig 1 (i)). These pits increase the effective surface area of exposed iron, thus making it more prone to degradation. Typically, pit formation in iron degradation is very slow due to the oxide passivation. This step is bypassed with the presence of magnesium. This not only increases the initial rate of degradation, but also the overall rate. The steady increase is due to the dynamic replenishing of magnesium sites as iron is corroded leaving magnesium from the depths of the samples once again exposed to SBF. The SEM micrographs taken post immersion study clearly show the differences between the three systems. In case of pure Fe, the salts form agglomerates on the surface and a few sites crack through and form shallow pit (Fig 1 (g)). Pure Mg experiences rapid corrosion due to its reaction with chlorides in the solution which further promote the reaction in that direction (Fig 1 (hi)). Mg also reacts with the phosphates in the solution to form amorphous calcium phosphate (ACP) which leads to white coloration of the sample along with hydroxyapatite (HAP) which is a mineral found in human bone. The Fe-Mg samples show a combination of these two with spots that show material removal (corresponding to Mg) and others showing salts agglomerates (Fe rich region). The stoichiometric chemical equation of magnesium reacting with water shows that 1g of Mg produces 1ml of H₂ gas (which is why hydrogen warts are common with Mg implants). Now, in our material as the direct availability of Mg is reduced, the production of hydrogen is also slowed down preventing the detrimental effects such as rapid pH increase and tissue damage.

CLINICAL RELEVANCE: The usage of permanent implants for temporary applications has unwarranted side effects such as infections, debris formation, stress shielding and even growth inhibition in specific cases. While these can be prevented by removal of implants, this demands multiple revision surgeries and the trauma attached to it. Usage of resorbable implants will solve all of these problems while also providing us with the opportunity to tune the degradation rate based on the bone. AM is the key to this new paradigm of biosorbable implants.