

Extended Abstract

Preparation of biodegradable iron scaffolds with controlled porosity for application in orthopaedic devices

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Abstract

Biodegradable materials for medical applications, that will naturally exit the physiological system after fulfilling their job, sound appealing so as to avoid problems caused by the long-time stay of an implant in the human body. For this purpose iron has been investigated since it is an essential element for the function of the human body. The most studied applications are in the cardiovascular field, and in this case, iron-based materials present the problem of having a degradation rate that is slower than the desired one. On the other hand, the degradation rate of iron may be suitable for the orthopaedic field, where a slower degradation rate is desired. There are very few studies on this matter, which suggest that this is an interesting area for investigation. The goal of this work is to study the suitability of using biodegradable iron for orthopaedic implant applications. An iron-based material has been developed by hot pressing and then characterized in terms of porosity, microstructure, mechanical behaviour and corrosion behaviour. The hot pressing technique has been proven to be suitable for processing iron and samples with porosity levels between 39 and 56% have been obtained by pressing at 100 MPa and sintering at temperatures up to 400 °C. The strength increases with sintering temperature up to 40 MPa, the corrosion rates achieved seem suitable for the application referred and the immersion tests show the formation of iron hydroxides as corrosion products while precipitation of calcium phosphates also occurs for the longer immersion periods. However, for those levels of biodegradability to be achieved a great compromise in mechanical properties had to be made, which, ultimately, made this material unsuitable for orthopaedic devices therefore, further research is recommended to be toward improving the mechanical properties of iron-based materials while controlling porosity and degradation rate.

Keywords: Iron, porosity, hot pressing, biodegradable orthopaedic implants

1. Introduction

Materials have been of great importance in the medical field and, with the evolution of technology, the search for better performing and safer materials have been increasing over time. Biomaterials and their applications go back as far as thousands of years in the history of mankind [1]. The use of metallic biomaterials had a big impulsion in the 1920s, with the invention of stainless steel [2]. Since then, several metallic materials have been developed and applied to the medical field.

The idea of biodegradable implants came with the awareness that many of the implants used in medicine are only needed to remain in the human body for a short period of time. The solution for that would be for the biomaterial to naturally degrade after fulfilling its objective [3]. Several materials have

been studied for this purpose, such as polymeric and metal based materials; nevertheless the metallic materials like iron and magnesium show the most promising outcomes [4-6].

Despite being the most popular materials for biodegradable implants, Fe and Mg still face some problems critical for the application: iron has a very slow degradation rate and magnesium degrades too fast. To overcome these problems research has been carried out involving alloying and structure modification but there is still a lot to be done to reach material properties adequate for the application [4]. Iron has not been studied as much as magnesium although it presents some important characteristics that are absent in magnesium and that are important, especially for orthopaedic applications, such as mechanical and degradation properties [5].

The question that arises is can an iron implant have the appropriate mechanical properties for a period of time sufficient to fulfil its purpose and then degrade in a non-toxic manner? The aim of this study is to investigate the possibility of developing porous Fe-based materials with increased degradation rate potentially able to be used as biodegradable scaffolds for orthopaedic applications. This study involves the preparation of Fe-based materials by hot pressing technique and the respective characterization in terms of porosity, microstructure, mechanical behaviour and biodegradation behaviour.

2. Methods

2.1 Sample preparation

The samples were produced by hot pressing using a Carbonyl Iron powder (Iron 99,5 %, $D_{50}=5\mu\text{m}$) as starting material. The hot press unit used for the experiments consisted of a conductive die surrounded by an induction coil, which generated heat by means of an electromagnetic field. This heat generation was independent of the applied pressure. The press used was a Carver M 3853 press equipped with heating plates (Carver M 2108.1). A Carver pellet die of 13 mm in diameter (model 3619) surrounded by a heating element Satec (1500 W) was used. A zinc stearate lubricant was applied to the walls of the die in order to avoid friction related problems. Hot pressing was carried out at a constant pressure of 100 MPa. With the aim of assessing the influence of temperature on the level of porosity achieved in the samples, three different processing temperatures were used: 100 °C, 200 °C and 400 °C. The hot pressing cycle consisted of heating the die to the desired temperature at a rate of 10°C per minute, followed by a period of 15 minutes for temperature stabilization. After that a uniaxial pressure was applied for one hour, followed by a cooling step.

2.2 Static corrosion tests

The samples for static immersion tests were mounted in epoxy resin, mechanically polished with SiC papers from 800 to 1200 grit, followed by cleaning with ethanol. The static immersion tests were performed by immersing the samples in Hank's balanced salt solution (Sigma H1387). A buffer was added, in order to maintain a pH value of 7.4. The tests were carried out at a constant temperature of 37.5 °C. Three batches of samples were prepared, each containing three samples from each of the three different temperatures used (100 °C, 200 °C and 400 °C). The first batch of samples was immersed for 7 days, the second one for 15 days and the last one for 30 days. After the tests, the samples were taken out of the bath and dried at room temperature. Note that for the purpose of this work, the immersion tests were meant for the determination of the corrosion mechanisms of the iron

samples. For a complete assessment of the material behaviour in the human body longer test periods are required.

2.3 Electrochemical corrosion tests

Electrochemical corrosion tests were performed under the same condition as in the static corrosion tests (the same solution, pH and temperature), using a 3 electrode cell with platinum as the auxiliary electrode and calomel as the reference electrode. For the electrochemical corrosion tests two samples were used: 200 °C and 400 °C. The samples were, previously mounted in epoxy resin, polished and spot welded to a conductive wire. The exposed surface area was 1 cm². Potentiodynamic curves were plotted from -0.5 to 0.5 V, at a scanning rate of 0,166 mV/s. The corrosion potential and corrosion rate were determined using the Tafel extrapolation method. In addition, open circuit potential curves were determined over a period of one hour and recording one point per second. These two curves constituted one cycle and the sample of 400 °C was exposed to three cycles and the 200 °C to two.

2.4 Diametrical compression tests

Mechanical degradation of the samples was evaluated by diametrical compression tests, also called "brazilian disc tests". This type of tests was used due to, not only the geometry of the sample, but also due to its extensive use to determine the strength in powder compacted materials [7-9]. The tests were performed on samples produced at different temperatures, both in the as-pressed condition and after the static immersion tests for 7, 15 and 30 days. A load cell of 10 kN was used, and the tests were carried out according to the ASTM D3967-08 standard [10].

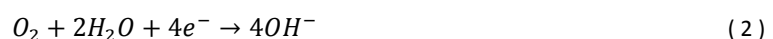
2.5 Microstructural characterization

The characterization of the microstructure of the samples prepared at different temperatures before and after the immersion corrosion tests for different times (0, 7, 15 and 30 days), was made by scanning electron microscopy (SEM) and x-ray energy dispersive spectrometry (EDS). The scanning electron microscope used was a JEOL JSM-6500F, combined with an EDS spectrometer INCA Energy, Oxford Instruments. This also allowed the identification of the corrosion products formed at the surface, contributing to an understanding of the degradation mechanisms occurring in these samples.

3. Results

3.1 Electrochemical behaviour

The potentiodynamic curves obtained for the samples pressed at 200 °C and 400 °C, before the immersion tests, are presented in *Figures 1*. The curves show the cathodic (*Eq. 2*) and anodic (*Eq. 1*) reactions occurring at the surface of the metal.



The cathodic reaction corresponds to the decreasing curve (the lower part of the curve), while the anodic one corresponds to the increasing curve (the upper part of the curve). When the behaviour changes from anodic to cathodic the corrosion current and potential are extrapolated and the corrosion rate can be calculated.

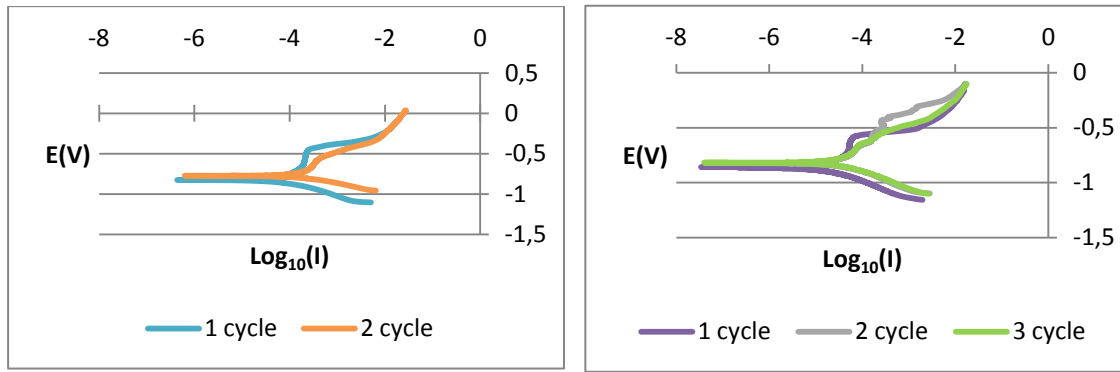


Figure 1: Potentiodynamic curves of samples pressed at: Left: 200 °C; Right: 400 °C.

The change in pH may have caused the formation of a passive film, which can be detected in the slope of the anodic curve in all the samples tested. After passivation of the metal the corrosion is dominated by pitting (non-uniform corrosion), which is not wanted. Despite that, it is still possible to determine the corrosion potential by means of the cathodic curve, and so the Tafel extrapolation method was still used to determine not only that, but also the corrosion current and the corrosion rate of the samples tested. The results are presented in *Table 1*.

Table 1: Results of the Tafel extrapolation method.

	E_{corr} (V)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	Corrosion Rate (mm/year)
400°C	-0,863	0,194	0,222
	-0,824	0,428	0,490
	-0,819	0,407	0,465
200°C	-0,770	0,017	1,927
	-0,825	0,881	1,009

From *Table 1*, it is possible to observe that the average values of the corrosion potential and current and the corrosion rate are higher for the samples pressed at 200 °C than for those processed at 400 °C. This happens because the samples pressed at 200 °C have higher porosity, which means that they have a larger surface area exposed to the corrosion medium. An enlarged corrosion area will make it easier for the medium to attack the samples and so, the corrosion rate will be higher. One can also notice that the difference in the corrosion potential values between the first and second cycles is significant. In fact, all the samples tested showed an increase in this value, meaning that there is a decrease in corrosion resistivity in the second cycle. This is due to the air in contact with the samples formed an oxide film on the surface, which constituted a protective layer against corrosion. After the first cycle that barrier was broken, making it easier for the metal to corrode in the following cycles [11, 12].

3.2 Microstructural characterization

The sample pressed at 100 °C shows a regular arrangement of undeformed and apparently unreacted powder particles (*Figure 2 a*). One can clearly see the spherical shape and sizes of the iron powder particles, indicating that the particles did not experience plastic deformation or interaction with each other during the processing stage at this temperature. On the contrary, the microstructures of the samples pressed at higher temperatures (200 °C and 400 °C) clearly show interconnections developed between powder particles, forming a porous network structure where only some of very small original powder particles can be distinguished (*Figure 3 a and 4 a, respectively*). The microstructures indicate that sintering of powder particles occurred at these temperatures with the

formation of bonds between them, which was not observed in the samples produced at the lower temperature.

EDS microanalysis on the as-pressed samples shows that the only element present in the surface layer of the samples is iron with traces of carbon, confirming that there was no contamination of the material during the pressing process.

The surfaces of the samples after the immersion tests were studied by using SEM and EDS. In *Figure 2* images of the surfaces of the samples produced at 100 °C before and after immersion for different periods are presented. The images show the corrosion products formed on the surface of the samples during immersion. After 7 days of immersion, a structure consisting of elongated particles was formed, which covered most of the samples' surface (*Figure 2 b*), and seemed to indicate a directional growth. In the sample immersed for 30 days, the surface is covered with small aggregates of particles with a powdery shape showing no specific orientation (*Figure 2 c*).

The results of EDS analysis of the corrosion products formed on the surface of the samples pressed at 100 °C after immersion, showed that they contain mainly oxygen and iron in their constitution, suggesting the formation of iron oxide. After 7 days of immersion, phosphorous, chlorine and calcium are also present on the surface of the samples, which suggests that compounds precipitated from Hank's solution. The elongated particles observed in SEM contained iron, oxygen, phosphorus and calcium. On the samples immersed for 30 days the presence of phosphorous and calcium is accentuated, however, chlorine was not detected on the surface of the sample. The presence of increased amounts of phosphorous and calcium in the sample immersed for 30 days suggests the formation of some form of calcium phosphate, that typically occurs in metal after immersion for long periods in Hank's solution [13-15].

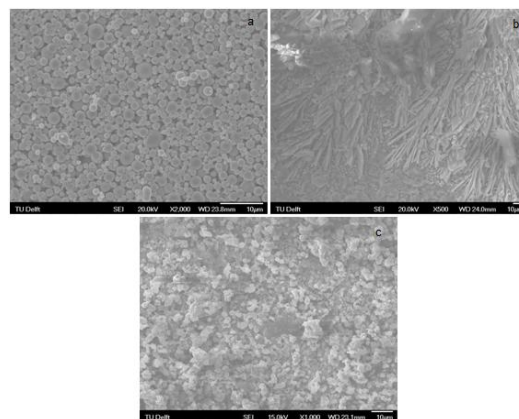


Figure 2: SEM images of iron processed at 100 °C: a) as-pressed; b) after immersion for 7 days; c) after immersion for 30 days.

Concerning the samples pressed at 200°C (*Figure 3*), the formation of directional structures on the surface was also observed. These structures are observed in samples immersed for 7 and 15 days (*Figure 3 b and c*). However, the morphology of the precipitates formed at the surface of the sample immersed for 30 days changes to aggregates of particles with a powdery shape, similar to those observed in the 100 °C sample immersed for the same period (*Figure 3 d*).

EDS analysis of the samples pressed at 200 °C also showed the presence of iron and oxygen for all immersion periods. On the samples immersed for 7 days, the presence of carbon, and phosphorous was observed. In the elongated particles on the surface, iron, oxygen and phosphorous

were the elements present. After 15 days of immersion the same elements are present on the surface of the samples, and evidence of sodium, potassium and calcium was also found. On the samples immersed for 30 days, the same elements were present, as in the samples collected after 15 days of immersion, with the exception of potassium, that was absent in these samples. As in the previous sample (100 °C) there is an increased amount of phosphorous and calcium in the precipitates formed at higher immersion periods, suggesting the formation of increased amounts of calcium phosphate particles. It is clear that, on one hand, these precipitates result from the oxidation of iron and, on the other, from particles (calcium phosphates) deposited from the Hank's solution. This is consistent with the results from the samples pressed at 100 °C, which showed similar elements on the surface. The samples pressed at 100 °C after 7 days of immersion showed similar elements as the samples pressed at 200 °C after 15 days of immersion, suggesting that the same corrosion mechanisms occurred on the surface of these samples, but at an accelerated corrosion rate.

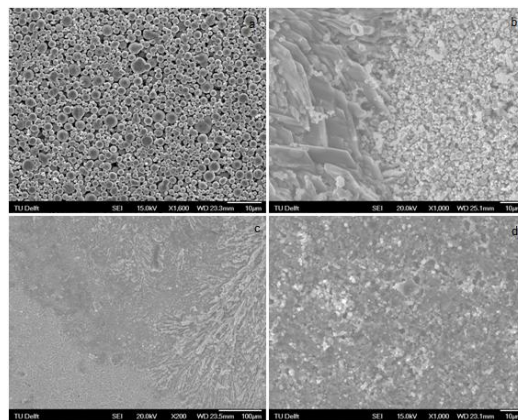


Figure 3: SEM images of iron processed at 200 °C: a) as-pressed; b) after immersion for 7 days; c) after immersion for 15 days; d) after immersion for 30 days.

The images obtained from the samples processed at 400 °C (*Figure 4*) also showed the formation of corrosion products on the surface. However, the morphology of the structures formed is different from that in the previous samples. After 7 days of immersion, the surface was covered with a dense layer of relatively small equiaxed particles (*Figure 4 b*). After 15 days of immersion, large hedgehog-like structures were present on the surface (*Figure 4 c*), that after 30 days of immersion tend to develop into fully grown columns, forming a rough layer that covered the entire surface (*Figure 4 d*).

The results of the EDS analysis of the samples processed at 400 °C after the different immersion periods, showed that after 7 days of immersion the corrosion products contained carbon, oxygen, sodium, phosphorous, potassium, calcium and iron in their constitution. This composition suggests the formation of a more complex precipitate or mixture of precipitates, containing probably calcium and iron phosphates, carbonates and oxides. However, the main difference to the previous samples is the presence of calcium and phosphorous, also after immersion for 7 days, which suggests a higher bioactivity of the current sample surface and probably a different corrosion mechanism. After immersion for 15 and 30 days, the same elements as in the previous processing temperatures were present on the surfaces of the samples, suggesting a regular mechanism of corrosion in this material for the different immersion periods.

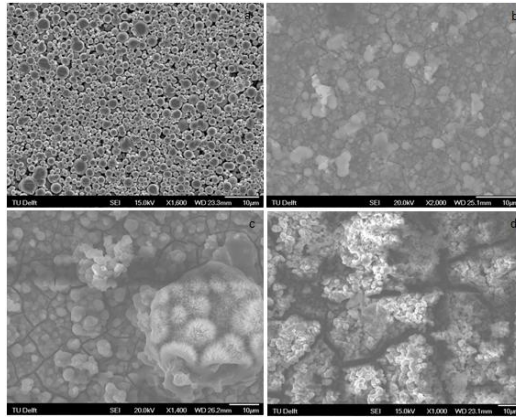


Figure 4: SEM images of iron processed at 400 °C: a) as-pressed; b) after immersion for 7 days; c) after immersion for 15 days; d) after immersion for 30 days.

3.3 Mechanical behaviour

The results of the compression tests are presented in *Figure 5*. For the as-pressed samples (corresponding to 0 days), bonding between particles will make the material stronger and so, the higher the processing temperature, the higher the material strength [8]. In *Figure 5* the increasing strength of the material with increasing temperature is obvious. It is clear that the samples pressed at 200 °C and 400 °C present a splitting strength about twice higher (18-20 MPa) than that produced at 100 °C (9 MPa). This is surely related to the microstructure of the samples produced at different temperatures, where it was clearly observed that only the samples produced at 200 °C and 400 °C developed structures with interconnectivity between powder particles.

The samples pressed at 100 °C show a slight increase in mechanical strength after 7 days of immersion, but after longer immersion times its resistance decreases again. The sample immersed for 30 days disintegrated even before the compression test and that is why it was not possible to test. Regarding the samples produced at 200 °C, the mechanical test results presented no significant variation in their mechanical strength after immersion for different periods of time. There is a slight decrease in strength after 7 days of immersion that then increases after immersion for longer periods to values closed to the as-pressed material.

On the other hand, the samples processed at 400 °C showed a considerable increase in strength after immersion for 7-15 days. The splitting strength reached a level of about 40 MPa, which suggests that reactions occurred on the surface of the material that caused the formation of molecules that have a binding role in the structure and contributed to these increased values of strength. However, immersion for a longer period of 30 days caused a decrease in strength, to the level of the as-pressed sample (20 MPa). This decrease should be expected due to increased exposure of the material to the corrosion medium.

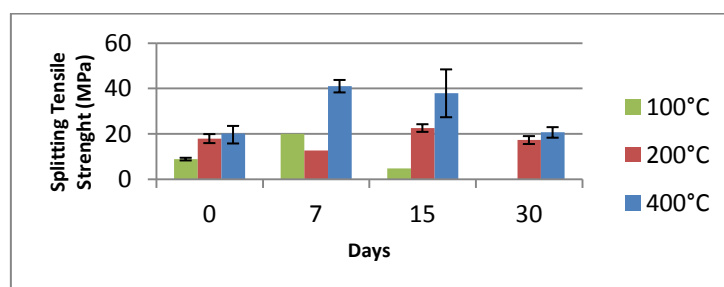


Figure 5: Results of diametrical compression tests.

4. Discussion

The results of as-pressed iron showed that different levels of porosity are possible to obtain in an iron-based material, using different processing temperatures, and the level of porosity decreases with increasing temperature due to increasing sinterability with this parameter. Hot pressing at 100 °C does not promote significant densification or consolidation of the material, however, pressing at temperatures of 200 °C and 400 °C causes an increase in the density of the samples, because exposure to higher temperatures softens the material, making it easier to deform by compression forces. At higher temperatures solid state diffusion processes at the particles interface occur, promoting bonding [16]. SEM images, along with electrochemical and mechanical tests seem to support this argument. In fact, the samples tested showed increasing strength with increasing processing temperature, since particles are more strongly bonded when pressed at higher temperature.

However, upon comparison with other studies conducted on this topic one can see that the initial strength of this material is too low. For the higher processing temperatures, the results obtained, showed a strength of 20 MPa while materials currently used for short-stay orthopaedic devices in the body require a minimum strength of 200 MPa [2, 6, 17-19]. Even when compared to the strength of the human bone, the values obtained in this work do not reach the strength necessary for an application in the cortical bone [2], which makes this material inappropriate for orthopaedic applications, in terms of mechanical properties. Sintering at higher temperature or a low degree of porosity would probably be necessary to obtain a material with the level of strength necessary for an orthopaedic application.

In what concerns the corrosion properties, the presence of porosity greatly increased the corrosion rate of the material. For the material processed at 400 °C, the results obtained are similar to the highest values for biodegradable iron found in the literature [12, 20]. As for the samples pressed at 200 °C, the results obtained doubled the ones obtained previously. These results show that the corrosion rate was definitely improved. However, when one combines the corrosion rates with the mechanical properties obtained in the materials developed in the present study, it is possible to conclude that, despite the good values obtained in terms of degradation, the mechanical properties were compromised and do not fulfil the requirements for orthopaedic devices.

The analysis of the precipitates formed on the surface of the iron samples after immersion suggests that two phenomena occurred: corrosion of the material with the formation of oxides and/or hydroxides; deposition of calcium and/or iron phosphates. The deposition of calcium phosphates occurs typically in materials submitted to long-term immersion in Hank's solution [13-15]. Both phenomena seem to be occurring in all the tested samples but at different levels of intensity. In the samples pressed at 100 °C and 200 °C for short period (7 days), mainly the formation of iron oxides/hydroxides occurs, with very little expression of phosphates formation (an Fe phosphate may form) [21]. Those precipitates didn't seem to affect the mechanical properties of the material, since results show no significant variations throughout time. This is confirmed by other studies conducted where the mechanical properties of iron are stable until they reach a point where they start to decrease and become compromised [22].

As the immersion time increases, both samples experience a higher density of calcium (and/or Fe) phosphate formation along with the formation of oxides/hydroxides. This is accompanied by a change in the morphology of the surface products from elongated particles into isolated powdery particles. Regarding the samples produced at higher temperature (400 °C), both phenomena also occur, but Ca (and Fe) phosphates formation occurs even for the short immersion period (7 days), revealing a more uniform overall mechanism of material degradation. The formation of precipitates is much more intense than in the previous samples, resulting in complete covering of the material's surface, which suggests a higher bioactivity of this sample.

The corrosion process of iron includes the formation of an unstable compound, ferritic hydroxide FeO(OH). The FeO(OH) compound has several phases and, depending on the surrounding environment conditions, such as oxygen concentration, salinity, pH, etc, some phases will have more tendency to form [23]. In fact, the chlorine content can affect the characteristics of the corrosion products in terms of structure and composition [24]. As found in previous studies [25], the phase with higher tendency to precipitate on the surface of the samples in the present study is the gamma phase (Y-FeO(OH)). The precipitated structures observed by SEM in this work are very similar to those of by Smith et al. [25], that studied the nucleation phenomenon of such structures in the presence of salt containing environment. The nucleation of directional structures on the surface (as observed in the samples processed at 100 °C and 200 °C at short immersion periods) allied with the formation of columns (as observed in the samples processed at 400 °C immersed for longer periods) are in good agreement with the existence of such mechanism in the samples tested in the present study. The conditions of the this study [25] were quite different from the ones presented in this thesis, however, a temperature and salinity dependence was noticed. The increased temperature and salinity seemed to accelerate the precipitation of the gamma phase on the surface. In the previous case, experiments were conducted in salt water at 50 °C. The structures started nucleating after 180 minutes and the columnar growth was present after 27 hours. Whereas, in this study, the temperature used for the immersion tests was 37 °C, and the concentration of salt in Hank's solution was lower than in salt water. Nevertheless, it is clear that a slower nucleation rate for the precipitate structures was found in the present study, taking 15 days for such precipitates to be observed and, 30 days for the columns to be developed. In another study on iron corrosion [24], performed at room temperature, the authors reported a period of 3 months for such structure to nucleate on the surface, which confirms the strong dependence of the precipitate formation on the solution temperature.

In conclusion, the corrosion rate of iron was improved by means of the incorporation of porosity in the samples, however, the compromise in mechanical properties was too extensive, making this material unsuitable to be used in orthopaedic applications.

5. Conclusions and future work

Samples of pure iron were prepared using hot pressing technique in order to find the suitability of this material as a biodegradable material for orthopaedic applications. Hot pressing was proven to be a suitable technique for porous iron-based materials. The degradation of these materials in Hank's balanced salt solution was evaluated and its mechanisms assessed. The results show that porosity improved the corrosion rate - the problem encountered in previous studies regarding iron as a

biodegradable material. However, the high levels of porosity and low temperature sintering resulted in materials with low strength that compromised their mechanical properties, making them unsuitable to be used as implant materials for orthopaedic devices.

A need remains to further investigate these materials. Future studies should focus on increasing mechanical properties of iron, while maintaining the corrosion rate achieved in this work. This could be accomplished by reducing the amount of porosity and by sintering at higher temperatures to improve the strength. Longer-term degradation tests should be carried out, also, in order to assess the material evolution during over the duration that it has to stay in the human body (about 1 year). Finally, cell compatibility tests should be performed, as well, so as to assess cell reactions to the corrosion products of the implant.

6. References

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