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Corrosion behaviour of metal fibre web structures

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Concerning the soft tissue reaction to stainless steel (316L) fibre mesh structures, it was found that mesh materials composed of small diameter fibres (2–8 μm) were lined by several layers of macrophages and giant cells. In addition, the majority of these mesh implants were filled with inflammatory cells. In contrast, mesh materials with a larger fibre diameter (12–22 μm) evoked less or no inflammatory reaction. An explanation for this observation could be the occurrence of shear displacements at the soft tissue–implant interface. In addition, corrosion phenomena as a result of the increased surface area of small fibre diameter meshes can be responsible for a greater toxic ion release. In this study the corrosion rates and the influence of shear stress on the corrosion rates of different stainless steel 316L fibre mesh structures were compared under *in vitro* laboratory conditions. It appeared that the effect of mechanical stress on 316L corrosion was a significant increase in the concentration of corrosion products in the loaded situation. Furthermore, the effect of fibre diameter on the release of corrosion products was a significant difference in ion release between mesh materials made of fibres with a diameter of 4 μm compared to meshes with a diameter of 12 and 22 μm. Therefore it was concluded that the chemical properties of fibre mesh implant material, together with the ability to release toxic ions, are an important determinant in the final tissue behaviour.

1. Introduction

Concerning the connective tissue response to subcutaneous implants, Campbell and von Recum [1] demonstrated that the surface texture of the implant was more important than the chemical composition. This finding was confirmed by a study [2] in which the authors evaluated the connective tissue response to three different sintered fibre web materials: (1) titanium fibre mesh; (2) stainless steel (316L) fibre mesh; and (3) Fe–Cr–Al alloy fibre mesh. After 12 weeks of implant healing, all tested materials showed a good biocompatible behaviour. In addition, the results appeared to indicate a relation between flexibility of the used fibre meshes and tissue reaction. Consequently, an additional experiment [3] was performed to test the hypothesis that the soft tissue response to fibre mesh materials can be influenced by changing the flexibility of these materials. For this study sintered stainless steel fibre web implants with varying flexibilities were used. This property was created by using different fibre diameters for the production of the meshes. The choice of stainless steel was based on the earlier observation that apparently the bulk composition of the mesh structure does not effect the surrounding tissue morphology. The implants were inserted subcutaneously into the dorsum of rabbits and left *in situ* for 16 weeks. It was found that mesh materials with a small fibre diameter (2–8 μm) were lined with several layers of macrophages and giant cells. In addition, the majority of these mesh implants were filled with inflammatory cells. In contrast, mesh materials with a fibre diameter of 12 or 22 μm evoked less or no inflammatory reaction. Inside the 22 μm meshes even young fibroblasts and blood vessels were present. Two explanations were given for this observation. First, the flexibility of the originally used meshes (22 μm) was already optimal. Second, the occurrence of shear displacements at the soft tissue–implant interface, together with corrosion phenomena as a result of the increased surface area of small fibre diameter meshes, are responsible for a greater ion release. Consequently, the toxic properties of these ions elicit the tissue response.

In the light of the above mentioned findings, the purpose of this study is to compare the corrosion rates and the influence of shear stress on the corrosion rates of different stainless steel 316L fibre mesh structures under *in vitro* laboratory conditions.

2. Materials and methods

2.1. Fibre mesh structures

For this study three different sintered stainless steel and one titanium fibre mesh material were used. Based on earlier reports about its corrosion resistance [4], the titanium mesh served as reference material. According to the information provided by the manufacturer the porous metallic fibre meshes were fabricated by interengaging and intertwining a multiplicity of metallic fibres. After compression the fibre structures

were sintered to bond the fibres at their points of contact. All mesh materials used for the experiments had a volumetric porosity of 86% and a weight of 600 g/m^2. The fibre diameters of the stainless steel were 4, 12 or 22 μm, while the fibre diameter of the titanium mesh sheet was 50 μm.

Before the experiment, the surface composition of all types of mesh sheets was analysed by energy dispersive X-ray analysis (EDS, Philips 525). The flexibility of the materials was determined as deflection per unit load in a three-point bending test as performed with a thermal mechanical analyser (Mettler TMA 40). Using the same equipment, the thickness of the various mesh materials was also measured. Furthermore, cross-sections of the meshes perpendicular to the direction of the fibres were made and examined with reflected light microscopy. By using computer-based image analysis (TCL-image) the circumference in proportion to the surface area of the fibres present in each cross-section was measured. The length of the circumference gives an indication of the potential contact surface of the different mesh materials. At least three specimens of each material were used for all measurements.

2.2. Corrosion testing method

Shear stress occurring during subcutaneous maintenance can disrupt the oxide film present along the metallic mesh fibres and cause fretting corrosion at the points of contact. This will result in the release of metal ions. Therefore, to simulate the effect of *in vivo* movement, the various metal fibre structures were tested under static and dynamic conditions. For both experiments, test specimens of 8 × 2 cm were used. The structure of the equipment used for the dynamic testing is shown in Fig. 1. The fibre mesh, together with a rubber sheet is fixed on a cylindrical tube (diameter 45 mm, height 30 mm) and placed inside a cylindrical container (diameter 50 mm, height 65 mm). On top of the mesh a spherical structure is placed and, after addition of test fluid, the container is sealed with a rubber sheet. The test specimens for the static experiments were placed in the same container as used for the dynamic conditions.

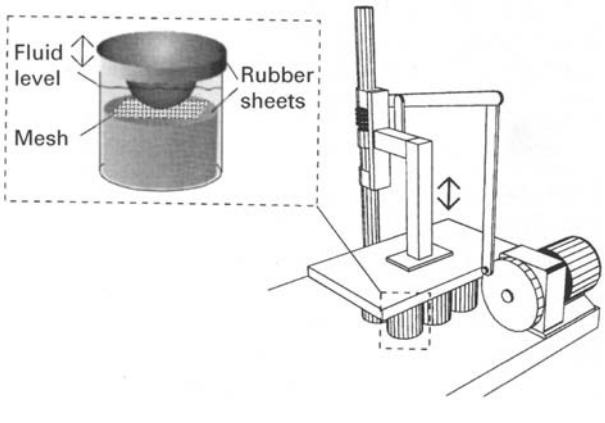


Figure 1 Structure of the equipment for the dynamic testing of the fibre mesh structures.

An apparatus, consisting of an a.c. motor and gear box with an eccentric rotating axis-system was connected to a crank-shaft. A horizontally placed plate was fixed to the crank-shaft. In this way cyclic external stress on top of the test containers could be provided by linear movement of the plate. The rotation velocity of the motor was 150 V rev/h. Cyclic external stress upon the upper rubber sheet will, through the sphere, provide stress on the fibre structure. Recovery of displacement was provided by the elastical properties of the rubber sheet at the lower side of the mesh until the consecutive moment of external stress appears again.

2.3. Corrosion test

Test sample coupons of the various mesh materials were prepared. One hour prior to the experiments, the materials were cleaned by ultrasonic vibration in 70% alcohol. Thereafter, they were rinsed with distilled water and air-dried.

After fixation of the test specimens, the static and dynamic fluid containers, as described above, were filled with 100 ml of medium. Three different incubation media were used: (1) 0.9% aqueous NaCl (solution of 9 g of extra pure sodium chloride powder in 1000 ml distilled water); (2) buffered lactate solution (0.9% aqueous NaCl with 40 g/l lactate acid, pH = 3); (3) buffered lactate solution with 10% fetal calf serum (Gibco).

All containers were covered with a rubber sheet to prevent evaporation and contamination. Subsequently, for the dynamic experiment the containers were fixed on a horizontal specimen holder and cyclic stress was applied over a period of 30 days as described above. The room temperature was kept constant at 37 ± 1°C. The static experiment was performed for the same experimental time and under the same environmental conditions. The tests were performed on two specimens of each type of fibre mesh in all three media.

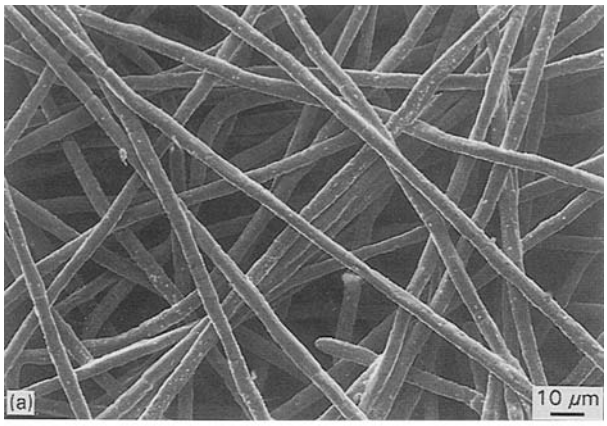
After 30 days the fibre mesh structures were removed from the test media and divided into two parts. One part was directly air-dried, the second part was rinsed with alcohol 70% to remove salt and protein precipitation and air-dried. Subsequently, the different specimens were prepared for scanning electron microscopy (SEM) and EDS.

The different test fluids were subjected to atomic absorption spectrophotometry (Varian AAS 775, Australia) to determine the concentrations of elements in the solutions. The spectrophotometer was calibrated before use with calibration curve points chosen depending on the expected range of the different element concentrations.

3. Results

3.1. Materials characterization

Fig. 2a and b are scanning electron micrographs of two 316L meshes, which show the surface aspects of the metal fibre structures. SEM analysis revealed that the surface of the 4 μm diameter metal fibres had a rather smooth appearance. On the 22 μm fibres



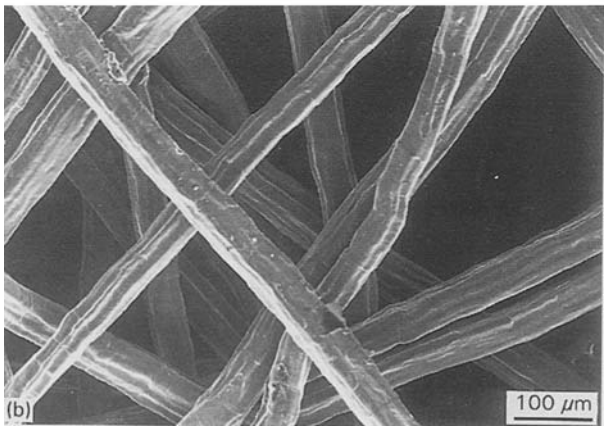


Figure 2 Scanning electron micrographs showing the surface aspects of the stainless steel 316L fibre structures: (a) 4 μm fibre; and (b) 22 μm fibre.

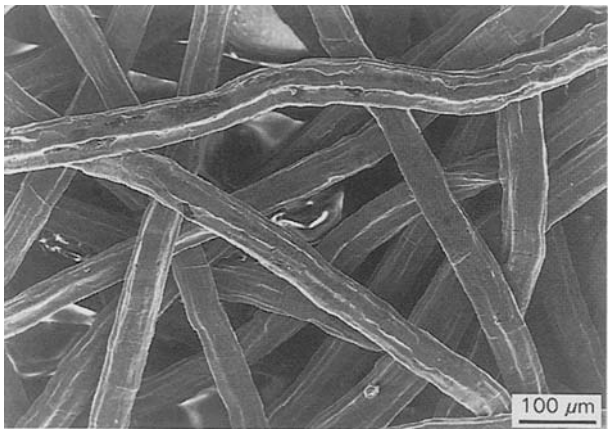


Figure 3 Scanning electron micrograph of the titanium fibres.

shallow longitudinal grooves were observed. Examination of the titanium fibres showed the presence of irregular, rather profound, longitudinal grooves (Fig. 3). After testing, SEM showed no changes in surface morphology of the different fibre structures compared to the micrographs taken before. In Table I the mean pore size, flexibility, thickness and circumference per area of the different fibre meshes are listed.

Table II gives the surface composition of the received mesh materials, as determined by energy dispersive X-ray analysis. It appeared that the stainless steel 316L mesh materials were composed of iron, chromium, nickel and molybdenum while the surface

TABLE I Characteristics of fibre web materials

Material	Mean pore size (μm)	Mean flexibility (μN)	Mean thickness (mm)	Circumference per fibre area (μm)
316L/4 μm	14.82	353	0.54	0.81
316L/12 μm	43.29	1300	0.54	0.35
316L/22 μm	43.68	673	0.53	0.19
Ti/50 μm	170.8	360	0.80	0.05

TABLE II Surface composition of mesh materials

Material	316L	Titanium
Iron (wt %)	70.1	0
Chromium (wt %)	19.1	0
Nickel (wt %)	8.3	0
Molybdenum (wt %)	2.5	0
Titanium (wt %)	0	100

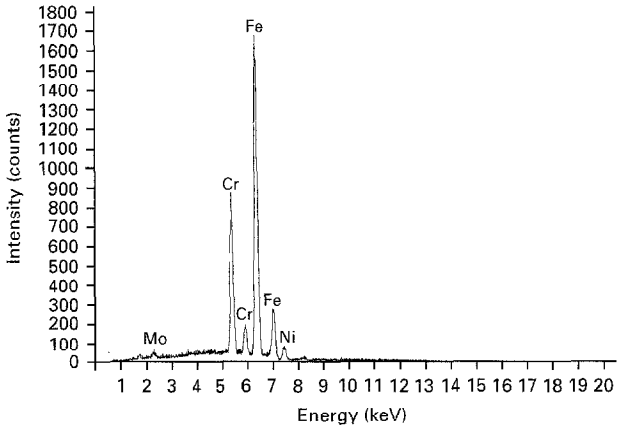


Figure 4 Energy dispersive X-ray analysis of a stainless steel fibre mesh after the experiments were performed.

of the titanium mesh was mainly composed of titanium. Fig. 4 shows the EDS spectrum of a stainless steel fibre mesh after the experiments were performed; no significant difference was noticed in surface composition before and after testing.

3.2. Atomic absorption spectrophotometry

Fig. 5a, b and c show graphically the concentrations of, respectively, iron, chromium and nickel measured in different media after testing the 316L mesh material. In none of the media was molybdenum detected. In the series of titanium experiments, no traces of titanium release could be found.

Considering the effect of different media, in 0.9% NaCl for all 316L materials, no substantial release of ions was observed, both in the static and dynamic situation. Further, there was a suggestion that the release of corrosion products was reduced in buffered lactate with serum compared to the buffered lactate. Statistical analysis, after pooling the different ion concentrations, revealed a significant decrease in ion release ($p < 0.001$) for meshes incubated in serum-supplemented lactate solutions.

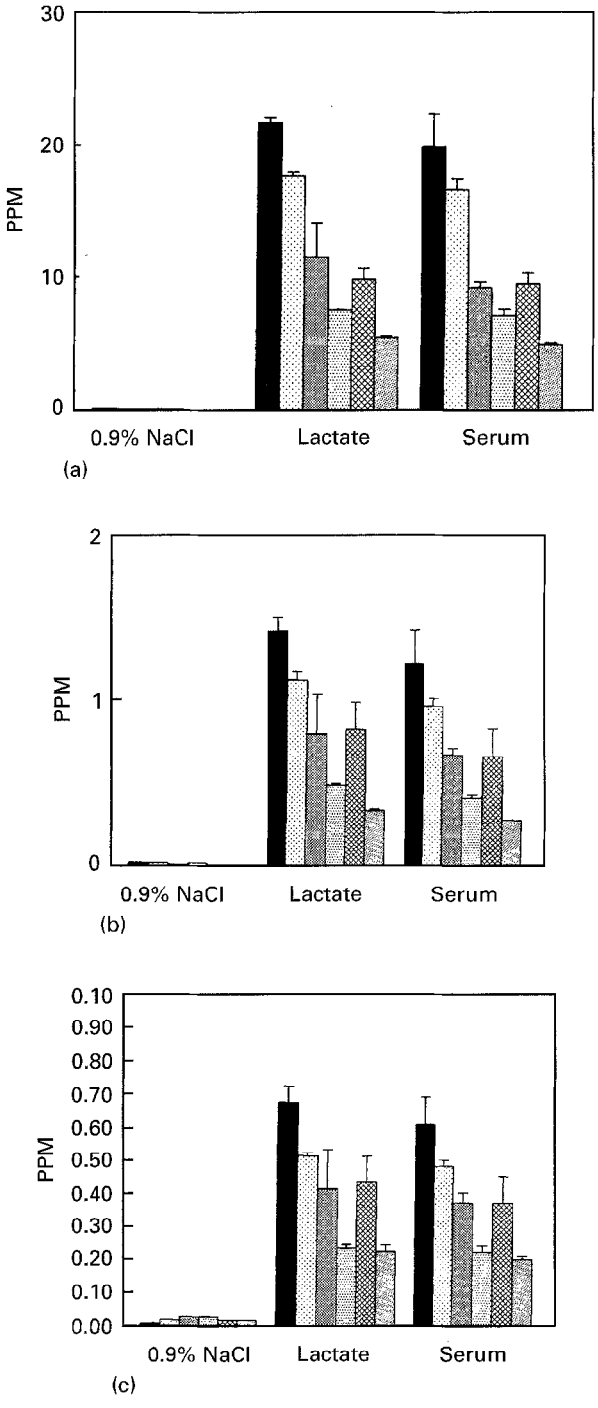


Figure 5 The concentrations of iron (a), chromium (b) and nickel (c) measured in the different media after testing the stainless steel 316L mesh material: ■ 4 μm, stress +; ▨ 4 μm, stress −; ▩ 12 μm, stress +; ▨ 12 μm, stress −; ▩ 22 μm, stress +; ▩ 22 μm, stress −.

To determine the effect of mechanical stress on 316L corrosion, all data for the static and all data for the dynamic testing situation were added. The Students *t*-test for the comparison of the means revealed a significant increase in the concentration of corrosion products in the dynamic situation ($p < 0.01$).

To examine the effect of fibre diameter on the release of corrosion products, a one-way analysis of variance (ANOVA) and a multiple comparison procedure (Newman–Keuls) was applied using the data as given in Fig. 5. The analysis showed a significant difference ($p < 0.01$) in ion release between the mesh materials made of fibres with a diameter of 4 μm compared to meshes with a diameter of 12 and 22 μm. The existence of a relationship between the fibre diameter and the release of corrosion products was confirmed by performing a simple linear regression test. The computed correlation coefficient varied from −0.6500 to −0.8189 for the fibre diameter using the data given in Fig. 5 with the strongest corelation for the amount of iron release. If we take the measured circumference per area of the different stainless steel 316L meshes, the computed correlation coefficient, varying between 0.7643 and 0.9133, shows an even stronger association between the variables.

4. Discussion

The aim of this comparative study was to investigate the corrosion behaviour of stainless steel 316L fibre mesh structures under laboratory conditions.

As this study showed, 316L meshes fabricated of fibres with a small diameter released significantly more corrosion products compared to meshes with a large fibre diameter. This phenomenon can be attributed to the larger surface area of meshes containing fibres with a small diameter [5]. In addition, the outcome of this study can be related to the results found in an *in vivo* experiment, where a correlation between tissue behaviour and fibre diameter of the various 316L stainless steel meshes was found [3]. It has to be noted that this is in contrast with Campbell and von Recum, who claim that the chemical composition of the implant is of minor importance compared to the surface geometry, as far as the tissue reaction is concerned [1]. Our experiment showed that although the bulk material is the same in the various mesh materials, the amount of corrosion products surrounding the implant markedly influences tissue behaviour.

Furthermore, it appeared that the test medium has an influence on corrosion rates. In contrast with 0.9% NaCl medium, a substantial ion release was observed, both under static and dynamic conditions, in lactate-containing medium. This phenomenon implies that factors other than shear stress alone are responsible for initiation of the corrosion process. The low pH of the lactate-containing media could be the trigger for this process. Because a low pH is also found in tissue surrounding an implant during the early stages of wound healing [6, 7], the corrosion process can be easily initiated *in vivo*. As our results show, addition of serum to the lactate solution reduces the corrosion rates significantly. Generally, the presence of serum proteins elevates the corrosion rates, although some *in vitro* experiments showed a marked reduction in fretting corrosion of stainless steel [8].

In contrast, the titanium meshes seem not to be affected by the different test media because no titanium could be detected. This low ion release may explain why the tissue reaction to these meshes, placed subcutaneously, is so good [2, 9]. In addition, the biocompatible behaviour of titanium exists because a highly adherent and protective oxide film forms around the surface of the metal implant [4, 10, 11]. Whenever titanium ions are released, by for example wear or shear stress, the extremely high affinity for

oxygen automatically takes care of the formation of electroneutral hydroxides and oxides. In contrast to our corrosion experiment, others have described high levels of titanium in tissue surrounding titanium implants, but it also appeared that this had little effect on tissue morphology and did not produce any clinical symptoms [12, 13], although it has to be emphasized that occasionally distant effects such as lymphadenopathy were reported [14]. Other metals, such as stainless steel or CoCrMo alloys, release corrosion products which are charged and not inert in tissue. This explains the tissue reaction observed in a previous study [3], although the amount of release of corrosion products also seems to be important for the tissue reaction.

In summary, the results of the present study show a correlation between the amount of corrosion products and the fibre diameter of the stainless steel mesh materials. It confirms our hypothesis that, apart from, for instance, surface texture, the chemical properties of the implant material are an important determinant in tissue behaviour.

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References

1. C. E. CAMPBELL and A. F. VON RECUM, *J. Invest. Surg.* **2** (1989) 51.
2. J. A. JANSEN, A. F. VON RECUM, J. P. C. M. VAN DER WAERDEN and K. DE GROOT, *Biomaterials* **13** (1992) 959.
3. J. A. JANSEN, J. P. C. M. VAN DER WAERDEN and Y. C. G. J. PAQUAY, *J. Mater. Sci. Mater. Med.* **5** (1994) 284.
4. S. G. STEINEMANN and P.-A. MAUSLI, "Titanium alloys for surgical implants-biocompatibility from physicochemical principles," Sixth World Conference on Titanium, 1988.
5. P. DUCHEYNE, M. MARTENS, P. DE MEESTER and J. C. MULIER, in "The cementless fixation of hip endoprostheses" (Springer-Verlag, Berlin, 1984) p. 109.
6. H. WOKALEK, *CRC Crit. Rev. Biocomp.* **4** (1988) 209.
7. M. SPECTOR, C. CEASE and X. TONG-LI, *ibid.* **5** (1989) 269.
8. S. A. BROWN and K. MERRITT, *J. Biomed. Mater. Res.* **15** (1981) 479.
9. Y. C. G. J. PAQUAY, J. E. DE RUIJTER, J. P. C. M. VAN DER WAERDEN and J. A. JANSEN, *ibid.* **28** (1994) 1321.
10. R. W. SCHUTZ and D. E. THOMAS, *ASM Metals Handbook* **13** (1987) 669.
11. K. H. W. SEAH and X. CHEN, *Corr. Sci.* **34** (1993) 1841.
12. A. B. FERGUSON, Y. AKAHOSHI, P. G. LAING and E. S. HODGE, *J. Bone Joint Surg.* **44** (1962) 323.
13. G. MEACHIM and D. F. WILLIAMS, *J. Biomed. Mater. Res.* **7** (1973) 555.
14. Y. SHINTO, A. UCHIDA, H. YOSHIKAWA, N. ARAKI, T. KATO, K. ONO, *J. Bone Joint Surg.* **75-B** (1993) 266.

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