Electrical Potentials between Stent-grafts Made from Different Metals Induce Negligible Corrosion

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WHAT THIS PAPER ADDS
Galvanic corrosion might, hypothetically, result in deterioration of a stent-graft. If this were the case, this would be disastrous for a patient after implantation of stent-grafts made from different metal alloys. Additionally, direct proof of whether electrical potential has any influence on damage to stent-graft frames has not yet been shown in previous studies. In our study, we detected that there was electric potential between the different stent-graft frames. However, negligible corrosion was found after 2 years of incubation. This fact makes the simultaneous deployment of stent-grafts with unmatched metal frames more acceptable.

Objective: Evaluation of the risk of galvanic corrosion in various stent-grafts in current practice, when devices with unmatched alloy compositions are deployed together.

Method: Five nitinol (NT) and two steel (SS) stent-grafts produced by different companies were used in different combinations to create 21 samples (NT:NT, n = 10; NT:SS, n = 10; SS:SS, n = 1). Electric potential was measured between the metal couplings after immersion in 0.9% NaCl at a temperature of 37 °C. Subsequently, the same samples were incubated for 24 months in 0.9% NaCl at 37–39 °C under hermetic conditions and examined under a scanning electron microscope in order to search for any evidence of corrosion.

Results: Electric potentials between different metals alloys were found (means: NT:SS, 181 μV; NT:NT, 101 μV; SS:SS, 160 μV). The mean electrical potential between stainless steel and nitinol samples was significantly higher than between NT:NT couplings (p < .001). During the final scanning electron microscope examination, only one spot of pitting corrosion (>10 μm) on a nitinol surface was found (associated with previous mechanical damage) in an NT:SS sample after 24 months of incubation in vitro and no sign of mechanical failure of the wires was found.

Conclusion: Direct contact between the stainless steel and the nitinol alloys does indeed create electrical potential but with a minimal risk of galvanic corrosion. No evidence was found for significant galvanic corrosion when two endovascular implants (stent-grafts) made from different metal composition were used in the same procedure.

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INTRODUCTION
Corrosion of nitinol and stainless steel is believed to be the reason behind damage to stent-graft frames while in the human body. Corrosion of nitinol alloy has been observed close to a platinum marker. Theoretically, electrical potential might appear between different metal alloys, thus causing corrosion. If this were true, the possibility for future mechanical failure would be dangerous for a patient with stent-grafts implanted with unmatched alloy frames. Direct contact between different metals after implantation of one stent-graft is not very common. This is because most of the stent-graft has an external nitinol frame and thus the fabric works as an electrical isolator. Nevertheless, different metals may accidentally make contact under the following circumstances. For example, if an additional stent or stent-graft is implanted into the proximal free flow of the first stent-graft to treat type I endoleak, or if a stent-graft iliac extension comes into contact with a stainless steel stent that has been implanted previously into the orifice of a common iliac artery. Such a situation has been observed while treating thoraco-abdominal aneurysms (by the chimney or branched techniques). Additionally, different types of metal might come into contact with each other if the fabric of the stent graft has become damaged. This situation might be especially common...
after implanting a bare stent into an iliac extension in cases of restenosis or bending of the stent-graft leg. Accidental unmatched alloy contact is observed after the simultaneous deployment of an XL stent to an aortic arch together with a stent-graft to the descending aorta in the case of its dissection. All the above-mentioned situations have occurred in our practice. Furthermore, no direct proof of electric potential and the presence of galvanic corrosion between different stent-grafts has yet to be confirmed, either in vitro or in vivo. Our study is therefore an attempt to bridge this gap in understanding. There were two basic aims: first, the measurement of electric potential between different metal alloys from different stents and stent-grafts after immersion in electrolyte solution; second, measurement of the corrosion on the surface of the samples after 24 months of in vitro incubation using a scanning electron microscope.

**MATERIAL AND METHODS**

We made use of seven samples from stent grafts and stents of five types: one sample from a Cordis stent (stainless steel, SS) (Cordis Corp., Hialeah, FL, USA), three from Gore (Gore 1, Gore 2, Gore 3) stent-grafts (nitinol, NT) (W. L. Gore & Associates, Flagstaff, AZ, USA), one from a Jotec stent-graft (NT) (JOTEC AG, Muri, Switzerland), one from a Medtronic (Minneapolis, MN, USA) (NT) stent-graft, and one from a Cook (Bloomington, IN, USA) stent-graft (SS). In order to create the samples for the experiment we took the rings from each stent-graft. Any fabric was removed completely. From these samples 21 couplings (test group) were created: NT:NT, 10 couplings; NT:SS, 10 couplings; SS:SS, one coupling. Additionally, seven couplings consisted of samples taken from the same stent-grafts creating the control group (Table 1). All of these were incubated under the same conditions (immersion in 0.9% NaCl solution at 37 °C). Electrical potential was measured between a metal coupling after 10 minutes of complete immersion, to achieve a stable and constant temperature at any part of the apparatus. In order to measure the voltage a Data-Logging System (DLS; Universal Data Login System BS85x version 5.1.0.4 Copyright© BTC 2002) was connected to a voltmeter (Brymen BM857a, BIALL, Gdansk, Poland). Characteristics of the measurement system were impedance/capacitance, 10 MO/30 pF; accuracy of voltage measurement, 1 µV. Gold electrodes, which allowed improved contact, were used to connect the measurement system to the metal couple, but were not immersed into the electrolyte (Fig. 1). A 1-mm-wide ebonite isolation spacer was utilized in order to maintain a small and constant space between the examined metals. Every measurement lasted 12 seconds and was repeated every 10 minutes initially up to a maximum of five times. (In the control group only one measurement was performed to confirm the lack of any potential differences.) If the five results differed by more than 10% more measurements were made until five results were obtained differing by less than 10%. The two most extreme values were then removed before calculation of the mean from all remaining values.

In the second part of the experiment incubation and further scanning electron microscopy was carried out on samples prepared from the stent-grafts which had been used for the voltage measurements. These samples were prepared by cutting out metal wires from both stent-graft frames (Fig. 2). The area to be examined by scanning electron microscope was 1 mm in length and was located in the middle of the sample. The margin of the examined area was marked mechanically using pliers with an impression. The average length of the wires in the sample varied between 7 and 10 mm.

The initial scanning electron microscope (20 kV, magnification 1,000× and 1,300×) was conducted using the marked areas of every wire. Afterwards the pieces of wire were connected with the use of a 5-0 Polypropylene surgical suture, using five throws to fix the sample (Fig. 2). All samples were immersed in 0.9% NaCl, making sure there was no air inside

**Table 1. Electric potentials between different metal couplings.**

<table>
<thead>
<tr>
<th>Alloy</th>
<th>NT</th>
<th>SS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stent-graft manufacturer</td>
<td>Jotec</td>
<td>Medtronic</td>
</tr>
<tr>
<td>NT</td>
<td>0 µV (n=1)</td>
<td>30 µV (n=5)</td>
</tr>
<tr>
<td>Medtronic</td>
<td>0 µV (n=1)</td>
<td>187 µV (n=5)</td>
</tr>
<tr>
<td>Gore 1</td>
<td>0 µV (n=1)</td>
<td>100 µV (n=5)</td>
</tr>
<tr>
<td>Gore 2</td>
<td>0 µV (n=1)</td>
<td>60 µV (n=3)</td>
</tr>
<tr>
<td>Gore 3</td>
<td>0 µV (n=1)</td>
<td>0 µV (n=1)</td>
</tr>
<tr>
<td>SS COOK</td>
<td>0 µV (n=1)</td>
<td>160 µV (n=5)</td>
</tr>
<tr>
<td>Cordis</td>
<td>0 µV (n=1)</td>
<td>0 µV (n=1)</td>
</tr>
</tbody>
</table>

Note: Green = control group (metal coupling from the same stent-graft; yellow = NT:NT, coupling with nitinol and nitinol; orange = NT:SS, coupling with nitinol and stainless steel; dark yellow = SS:SS, coupling with stainless steel and stainless steel; n = number of voltage measurements; NT = nitinol; SS = stainless steel; SD = standard deviation.
the 20-mL test tubes which were then hermetically sealed. In our experiment we used a scanning electron microscope manufactured by JEOL (version JSM 6100, acceleration voltage 5–35 kV, gun type Tungsten & lab 6; Warsaw, Poland). The 21 test tubes were incubated for 2 years in a controlled environment (37–39 °C, darkness), in an incubator with an environmental control system armed with alarms (acceptable temperature variation 2 °C). A final scanning electron microscope examination was then made as before. In both scanning electron microscope examinations spots of pitting corrosion >10 μm were looked for.6–8

Statistical analysis

Data were analyzed using a commercial statistical software package (Statistica Pl software; version 5.0.97). The Mann–Whitney test was used for comparisons between NT:SS, NT:NT combinations and SS:SS due to non-normal distribution. A p value <.05 was considered statistically significant.

RESULTS

Electric potentials from the 21 metal couplings are present in Table 1 (in total 95 voltage measurements were made) and group means in Table 2. The voltage between the examined metal pairs varied, depending not only on the metal alloy but also on its producer. However, there was no potential between pieces of metal taken from the same stent-graft (control group). The highest voltage was found between NT:SS couplings: The average potential between nitinol and stainless steel was 181 μV, but the maximum potential reached over 250 μV. A statistically significant difference was found only between the group of NT:SS and NT:NT couples (181 μV versus 101 μV, respectively p < .001) and not between the other combinations (NT:SS vs. SS:SS or NN:NN vs. SS:SS couples).

The initial scanning electron microscope examination did not show any signs of corrosion. An example of the initial scanning electron microscope examination is present in Fig. 3A. The final scanning electron microscope examination revealed only one spot of pitting corrosion on a Medtronic nitinol stent-graft which was part of an NT:SS

Table 2. Electrical potential from nitinol and stainless steel alloy combinations.

<table>
<thead>
<tr>
<th>Metal combinations</th>
<th>n</th>
<th>Mean voltage (μV)</th>
<th>Median voltage (μV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NT:NT</td>
<td>44</td>
<td>101.11</td>
<td>91.5</td>
</tr>
<tr>
<td>SS:SS</td>
<td>3</td>
<td>160</td>
<td>160</td>
</tr>
<tr>
<td>SS:NT</td>
<td>48</td>
<td>181.15</td>
<td>175</td>
</tr>
</tbody>
</table>

Note. n = number of voltage measurements; NT:SS = couplings between nitinol and stainless steel; NT:NT = nitinol and nitinol; SS:SS = stainless steel and stainless steel.
DISCUSSION

The likelihood that different metals may come into contact with each other with the use of stent-grafts is rare but increasing. At our practice the typical situation when an unfavorable connection occurs is after the treatment of endoleaks as mentioned in the Introduction. This can be due to either accidental damage to the fabric after implanting a bare stent into a stent-graft, or to intentional alloy contact, for example after implantation of a stent into the free flow of the stent-graft or after using the chimney/branched techniques in the treatment of the thoraco-abdominal aneurysm. A further possibility for accidental metal contact might occur if a nitinol self-expandable stent has to be implanted into the iliac artery after its angioplasty. If a stent-graft with an internal frame (e.g. Powerlink, EndoFit, or AFX) was previously implanted this would result in the accidental contact of unmatched alloys. The opposite case has also been noted (namely a steel stent already present in iliac common artery covered by a stent-graft extension with an external nitinol frame). Reducing the profile to cross challenging iliac arteries is a current practice nowadays. There are reported combinations, for example low profile Zenith LP bodies (16 Fr) with spiral Z limbs (14—16 Fr), or other inter-manufacturer combinations, for example Cook Zenith LP body with Gore 27-mm flared limbs.9

Another area in which this situation might happen is in the process of revascularization of the visceral arteries, if they have been accidentally covered after the implantation of a stent-graft to an abdominal aortic aneurysm (using the bail-out technique). In such situations, the covered stent with an external metal frame (e.g. Viabahn) that has been implanted to a visceral artery (e.g. renal artery) comes into contact with the frame of the stent-graft.

It is because of the increasing frequency of this situation that the authors wanted to investigate the probability of accidental creation of a galvanic cell between different vascular implants, preferably before these occur (note that at present there are no reports yet of any corrosion-damaged stent-graft frames.) The EUROSTAR registry has only reports of stent-graft failures due to fabric damage. (Theoretically mechanical flexion and extension of the frame due to the pulsating action of the arterial walls could also cause damage to the stent-graft frame.) Nevertheless, pitting corrosion has indeed been observed in explanted stent-grafts and perhaps it is just too early for such a complication yet.1—3

Possibly steel could be one cause of the creation of a galvanic cell and subsequent (theoretically) triggered galvanic corrosion. This idea was postulated after the discovery of focal corrosion of nitinol close to platinum markers.1,4 Is galvanic corrosion responsible for such findings? To search for an answer to this question, one needs to first ascertain whether metal couplings between different implants really can give rise to electric potentials. Electric potentials were therefore measured between metal alloys immersed in an electrolyte. Instead of using human blood, a 0.9% solution of NaCl was chosen for the following reasons: first, it is easier to use saline than blood; secondly, it is isotonic with serum and is a very stable electrolyte (between concentrations of 0.5% and 2.5%).6,7,10 Moreover, other ions added to the saline solution (e.g. potassium, magnesium) do not change this.8 Accordingly, 0.9% NaCl, rather than Ringer’s lactate, Hartmann’s solution, or another electrolyte, appears to be the medium of choice in this type of experiment.

Measurement of the potential between the metal alloys was not so simple. It was decided to measure the potentials using interrupted repetition instead of one single measurement, to allow for fairly large fluctuation in the potential during the time of immersion. Previous research has shown that potentials between metals in saline solutions (at concentrations between 0.5% and 2.5% and temperatures between 20 °C and 80 °C) increased slightly within the first hour (about 10%) and afterwards became stable over a longer period of time.6,7,10 Thus in our study a 10% difference in the voltage measurements was accepted. The system was very sensitive to disturbances within the environment such as a mobile phones, the turning on of a microwave oven in the next room, or a car running outside the building. The risk of such disturbances is reduced when the experiment is conducted during a shorter period of time and every measurement lasted only 12 seconds (in any case the potential always achieved a plateau after 3—6 seconds).

The presence of an electric potential between different metal alloys was not surprising. Measurement of electric potentials between similar metal alloys was, however, surprising. A difference in potential was found not only between similar alloys from different brands but also between the same alloys from the same producer. This shows that the alloys used in the production of stent-grafts vary, even from one producer. Note that no electrical potential was measured between pieces of metal taken from the same stent graft (Table 1).

The stent-grafts that we have used in our experiments have come to us over a period of about 5—7 years. It is possible that during this time the producers have changed their alloy supplier, and as a consequence now manufacture their stent-grafts from different alloys mixtures, composed of nitinol or stainless steel. The composition of nickel and titanium in the nitinol alloy will slightly change every time it is created (and similarly for stainless steel; note that the nitinol producer remains unknown and therefore cannot be contacted). This therefore is of further concern and raises a further question: Is it safe to perform simultaneous implantations using devices from the different lots purchased from the same manufacturer?

The values of electrical potentials measured between different alloys were much lower than those thought necessary to cause galvanic corrosion. Wranglem11 and Roberge12 state that in order to trigger galvanic corrosion more than 100—300 mV potential (according to the anodic index) is needed. This is around 1,000 times higher voltage than has been measured in our study.

The question then remains: Why has pitting corrosion been seen close to platinum markers in a previous study?1 This should be clarified in order to avoid a problem of corroded...
stent-graft failures during the next 20–30 years. It seems especially urgent considering the following two possible phenomena. The first phenomenon is called a “lasagna cell” and might happen because one frame of a stent-graft comes into contact with another within a small area where galvanic corrosion is concentrated. In this way corrosion might occur rapidly even under the influence of a very small electrical potential. A similar situation can be observed when salty food (an electrolyte) is stored in a steel pan (the cathode) and is covered with aluminum foil (the anode).

The second phenomenon is called “pitting corrosion” and is observed on the surface of metal due to damage to its passive external layer. This area becomes anodic (depasivation), leading to very localized galvanic corrosion. Depassivation of the metal layer is more likely if the surface of the metal has a scratch, which might occur at the place of contact between the frames of two stent-grafts. The above phenomena cause the corrosion to be significant even with very small potentials, which motivates us to pursue this research further.

Stent-grafts producers try to use corrosion-resistant alloys (with the lowest anodic index) and of course various technical methods to protect the metal alloys against corrosion. Different alloys have a different anodic index due to their various components. Generally, manufacturers of the implants choose the metal for their products based on “corrosion-free” grades, for example stainless steel implants are usually made of austenitic alloy 316L (X2CrNMo17-12-3) and these alloys are especially resistant to corrosion. Consideration might, however, also be directed towards superaustenitic stainless steels, which exhibit an even higher resistance to chloride pitting and crevice corrosion, but are more expensive. We cannot at present advise an alloy of choice for currently used sent-grafts as we do not know at present the conditions or prevalence of galvanic corrosion.

In any case, nowadays most producers use nitinol in their products, not because of its small anodic index (about 0.3 V), but because of its mechanical features. Nitinol frames which have an appropriate radial force have been made of much thinner wires than similar stainless steel products, and thinner wires are the only way towards miniaturization. It has been observed that many vascular surgeons experience complications while passing a stent-graft into a very narrow or calcified iliac artery, and any rupture of the artery coupled with severe retroperitoneal bleeding causes the endovascular approach to be abandoned and forces the surgeon to pursue open surgery. It is to avoid such situations that the producers make the delivery system as thin and elastic as possible.

Furthermore, nitinol also has a natural resistance to corrosion. It is through the natural corrosion of the nitinol surface that thin layers of titanium oxide protect the nitinol from further deterioration, although a small scratch on the surface might trigger pitting corrosion which would destroy this passive layer. There are some additional ways to protect nitinol and stainless steel wires including polishing or amorphorization (oxide coating), PSII surface modification, ultrasonic cleaning, or covering with silicon. Further techniques could include the use of extra sacrificial anodes, which have been placed within the stent material to prevent galvanic corrosion, or by using an extra fabric cover on the stent-graft frame. The limitations to these are the size of the delivery system. This entails that the whole system must be as simple as possible, and made of the smallest mass of metal and fabric in order to create the possibly of the thinnest delivery system. This therefore, at present, excludes several of the aforementioned methods of protection.

Any electric potential between unmatched alloys, together with the possibility of phenomena such as pitting corrosion or “lasagna cells” and the needed trend for miniaturization of stent grafts, gives rise to an obvious question: Is galvanic corrosion a problem which must be taken into account? Or can it be forgotten about?

The only ways to answer this question are either to wait and see if stent-grafts corrode and fail in the human body in the future (which involves a risk of an unknown proportion of failures), or to try to create conditions in vitro of (perhaps accelerated) galvanic corrosion to be measured by scanning electron microscopy.

Previous investigation showed that corrosion of the nitinol was even more aggressive in the saline solution rather than in the fluid environment of the human body. A 2-year incubation period should be long enough to check for any symptoms of corrosion, because evidence of pitting corrosion was found in explanted stent-grafts after 2–4 years of implantation.

One problem in our study was to achieve stability of the incubation. First, changes in the concentration of the solution needed to be avoided (no water evaporation, hermetic closure). Secondly, the temperature ought to be kept stable (total darkness to avoid the influence of the light on medium temperature, control of the temperature with an acceptable fluctuation limit up to 2 °C). Thirdly, the stability of electric potentials in NaCl solution is also vital. This is because it has been shown that 0.9% NaCl in 37 °C keeps electric potentials stable over a long period.

The comparison between the initial and final scanning electron microscope examination revealed the presence of pitting corrosion only in one place on a nitinol sample. The definition of the criteria for corrosion (visible pitting corrosion > 10 μm) was simple and based on another experiment as well as the fact that corrosion changes are usually larger than 10 μm. However, only one new spot of pitting corrosion was recorded in the final scanning electron microscope examination without any evidence of mechanical failure of the wire. Moreover, it is hardly worth postulating that this change has anything in common with galvanic corrosion, as it was found in an area marked by the pliers. It is possible that damage from the pliers actually triggered the corrosion encouraging the mechanism of depassivation, causing further damage to the surface. No evidence of the potential risk of the “lasagna” phenomenon was found.

This can be regarded as the first direct in vitro experiment to study this phenomenon. Despite all the mentioned limitations the revealed results are nonetheless important
from the clinical point of view. This is especially the case because unmatched alloy deployment is occurring more and more frequently because of the constantly rising number of endovascular procedures. These results seem to point to the fact that we are probably not going to experience a rising numbers of corroded stent-grafts within the next two or three decades.

Despite the fact that the reasons behind stent-graft frame corrosion still remain unclear, it is nonetheless a situation that will encourage further investigation in the future. In conclusion, close contact between stainless steel and nitinol stent graft frames do create electrical potentials but with a minimal risk of galvanic corrosion after 2 years of incubation.

CONFLICT OF INTEREST
None.

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