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Project #: E-18-694   Cost share #:   Rev #: 4
Center # : 10/24-6-R8025-0A0   Center shr #:   OCA file #:
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Contract#: AGREEMENT DTD 12/22/93   Mod #: 2   Document : AGR
Prime   #:   Contract entity: GTRC

Subprojects ? : N   CFDA:
Main project #:   PE #:

Project unit: MSE   Unit code: 02.010.112
Project director(s):
   MAREK M I   MSE   (404)894-2380
                                                                    |

Sponsor/division names: C R BARD INC   / BILLERICA, MA
Sponsor/division codes: 202   / 135

Award period: 940101   to   961231 (performance)   961231 (reports)

Sponsor amount   New this change   Total to date
     Contract value   80,000.00   117,475.00
     Funded   80,000.00   117,475.00
Cost sharing amount   0.00

Does subcontracting plan apply ?: N

Title: ELECTROCHEMICAL STUDIES OF IMPLANT MATERIALS

                    PROJECT ADMINISTRATION DATA

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Security class (U,C,S,TS) : U   ONR resident rep. is ACO (Y/N): N
Defense priority rating   :   supplemental sheet
Equipment title vests with: Sponsor   GIT
   NONE PROPOSED
Administrative comments -
   MOD 2 AWARDS ADDITIONAL FUNDS AND EXTENDS THE PERIOD OF PERFORMANCE

GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION

NOTICE OF PROJECT CLOSEOUT

Closeout Notice Date 01/10/97

Project No. E-18-694_____   Center No. 10/24-6-R8025-0A0_

Project Director MAREK M I_____   School/Lab MSE_____

Sponsor C R BARD INC/BILLERICA, MA_____

Contract/Grant No. AGREEMENT DTD 12/22/93_____ Contract Entity GTRC

Prime Contract No. _____

Title ELECTROCHEMICAL STUDIES OF IMPLANT MATERIALS_____

Effective Completion Date 961231 (Performance) 961231 (Reports)

Closeout Actions Required:	Y/N	Date Submitted
Final Invoice or Copy of Final Invoice	Y	_____
Final Report of Inventions and/or Subcontracts	N	_____
Government Property Inventory & Related Certificate	N	_____
Classified Material Certificate	N	_____
Release and Assignment	N	_____
Other _____	N	_____

Comments_____
_____

Subproject Under Main Project No. _____.__

Continues Project No. _____

Distribution Required:

Project Director	Y
Administrative Network Representative	Y
GTRI Accounting/Grants and Contracts	Y
Procurement/Supply Services	Y
Research Property Managment	Y
Research Security Services	N
Reports Coordinator (OCA)	Y
GTRC	Y
Project File	Y
Other _____	N
_____	N

Quarterly Report

LONG-TERM CORROSION RATE OF PROSPECTIVE IMPLANT ALLOYS IN RINGER'S SOLUTION

Submitted to

C.R. Bard, Inc.
1200 Technology Park Drive
P.O. Box 7025
Billerica, MA 01821

by

Miroslav Marek, Ph.D.
Professor
School of Materials Science and Engineering
Georgia Institute of Technology
Atlanta, GA 30332-0245

April 5, 1995

Objective and Materials

Long-term electrochemical corrosion tests two prospective implant alloys have been performed. For the corrosion tests the wire specimens were exposed to Ringer's solution, saturated with an atmosphere of 6% oxygen, 5% carbon dioxide and balance nitrogen, at 37°C. The pH of the solution was adjusted at 7.4.

Methodology

Two types of electrochemical tests were performed. The first technique essentially follows the procedure described by Postlethwaite, 1981.[1] In this test the specimen is exposed to an electrolyte containing dissolved oxygen, and the electrode potential is measured. The potential is then maintained, using an electronic potentiostat, at the same value (corrosion potential), and the dissolved oxygen is removed by deaeration with pure nitrogen, thus eliminating the cathodic current of oxygen reduction. The controlling current is then equal to the anodic current, which is proportional to the corrosion rate. In this series of tests the current during the measurement period was integrated, and the average current was determined by dividing the integrated current (charge) by the time of the measurement period (usually 1 hour).

The second test methodology was the measurement of the polarization resistance, which is inversely proportional to the corrosion rate. The measurements were performed using the technique of Electrochemical Impedance Spectroscopy (EIS). Since the results do not provide directly the corrosion current density, and the calculation of the corrosion rate requires the knowledge of the Tafel constants, the corrosion rate results were obtained for several assumed values of Tafel constants in the range commonly observed, and also compared with the polarization results.

Results

A. Polarization current density measurements

Two long term polarization tests of each material have been performed. Both materials showed a sharp drop in the corrosion current density from the initial values, and stabilization at a nearly constant current density at longer exposures. The mean current densities after one day exposures were on the order of 10^{-8} A/cm^2. The average current densities calculated for all exposures of 17 days and longer, when the current density was relatively stable, were in the range of 2 to 5×10^{-9} A/cm^2.

B. Polarization resistant measurements by EIS

Tests of two specimens have been completed. The data show an increase in polarization resistance with exposure time, consistent with the inverse relationship between polarization resistance and corrosion current density.

[1] J. Postlethwaite, "Direct Measurement of the Corrosion Current for Oxygen-Reduction Corrosion," in *Electrochemical Corrosion Testing*, ASTM STP 727, F. Mansfeld and U. Bertocci, Eds., ASTM, 1981, pp. 290-302.

The polarization resistance R_p is related to the corrosion current density i_{cor} as follows[2]:

$$R_p = B/2.3\ i_{cor} \qquad (1)$$

where B is a numerical parameter, which is a function of the polarization (Tafel) constants b_a and b_c as follows:

$$B = b_a\ b_c\ /(\ b_a + b_c) \qquad (2)$$

When the constants b_a and b_c are not known, as in this case, the parameter B can be estimated, based on the knowledge of usual values of the constants. When the electrode is in an ideally passive state and the current density is totally potential independent, B is equal to b_c. Since both the polarization test data and the polarization resistance data showed nearly constant values for longer exposures, the average current density for all exposures of 17 days and longer, when the current density was relatively stable, was then used to calculate the parameter B.

Metal ion dissolution

The electrochemical tests do not provide means for identifying the dissolving species or their distribution. One possible assumption is that the elements dissolve in the proportion of their concentration in the alloy. If one element is considered critical, a worst case assumption is that the dissolution of this element is responsible for all the measured corrosion current density.

To obtain a single elements dissolution rate corresponding to current density, Faraday's law is used[3],

$$m = i\,t\,A/n\,F \qquad (3)$$

where m is the reacted (dissolved) mass per unit area, i is current density, t is time, A is atomic weight of the element, n is the change in the oxidation state (ionic charge of the element dissolved), and F is Faraday's constant (96,493 C/equivalent). The dissolution rate[3] of an element

$$r_i = m/t = i\,A_i/n_i\,F \qquad (4)$$

If the assumption is that the alloying elements dissolve proportionately to their concentration in the alloy, the total charge per unit time (product $i_{avg}\,t$ in equation (3)) must be partitioned. The partitioning coefficient k_i

$$k_i = ((x_i\ n_i/A_i)/(\Sigma\ (x_i\ n_i/A_i)) \qquad (6)$$

where x_i is the number of grams of an element in a unit mass of the alloy, and A_i, n_i are the atomic weight and oxidation state, respectively, for each major alloying element. The average daily release rate of an element is then calculated as follows:

$$r_i{}' = (\ i_{avg}\ k_i\ A_i\ /\ n_i\ F)\ 8.64E4\ s/day\quad [g/day] \qquad (7)$$

---

[2] J.C. Scully, *The Fundamentals of Corrosion*, 2nd ed., Pergamon Press, 1975, p. 86.

[3] D.A. Jones, *Principles and Prevention of Corrosion*, Maxmillan Publishing Co., 1992, p.75.

Quarterly Report

PRELIMINARY CHARACTERIZATION OF THE ELECTROCHEMICAL CORROSION BEHAVIOR OF PROSPECTIVE ALLOYS IN RINGER'S SOLUTION

Submitted to

C.R. Bard, Inc.
1200 Technology Park Drive
P.O. Box 7025
Billerica, MA 01821

by

Miroslav Marek, Ph.D.
Professor
School of Materials Science and Engineering
Georgia Institute of Technology
Atlanta, GA 30332-0245

July 26, 1995

Objective

The objective of the test program was a preliminary evaluation of the corrosion susceptibility and behavior of specimens of three new prospective alloys in a simulated human body environment.

Materials

The specimens included wire specimens of three alloys of similar composition, Coded A, B and C, supplied by C.R. Bard, Inc

Test Program

The test program consisted of limited electrochemical characterization using corrosion potential and potentiodynamic anodic polarization measurements. Exploratory crevice repassivation tests were performed for Code A alloy.

Test specimens

For testing the specimens were in the form of a loop immersed in the solution. The exposed area, determined for each wire size, ranged from 0.85 to 1.5 cm^2.

Test media

For the corrosion potential and anodic polarization tests the specimens were exposed to Ringer's solution adjusted to 7.4, at 37°C. The composition of the solution was as follows:

NaCl	9.0 g/L
CaCl$_2$.2H$_2$O	0.17 g/L
KCl	0.4 g/L
NaHCO$_3$	0.2 g/L

For corrosion potential measurements the solution was saturated with an atmosphere of 6% oxygen, 5% carbon dioxide and balance nitrogen. For the anodic polarization tests the solution was deaerated using a high purity nitrogen gas. The crevice repassivation tests were performed using 0.9% sodium chloride solution, exposed to air.

Test procedures

Corrosion potential tests.--The specimens were tested in a two-electrode glass cell, jacketed for temperature control by circulation of water from a constant-temperature circulator. The potential was measured with respect to a Saturated Calomel Electrode (SCE). The equipment consisted of an electronic potentiostat controlled by a microprocessor (Model 351, EG&G Princeton Applied Research, Princeton, NJ). The potentials were measured for exposure periods ranging from 24 to 92 hours, starting immediately after filling the cell with the solution.

Anodic polarization tests.--The specimens were tested in a three-electrode glass cell, temperature-controlled at 37°C. A Saturated Calomel Electrode (SCE) with a salt bridge and a Luggin capillary was used as a reference, and a platinum wire as counter-electrode. The equipment consisted of an electronic potentiostat controlled by a microprocessor (Model 351, EG&G Princeton Applied Research, Princeton, NJ). Potentiodynamic polarization curves were recorded at a potential scanning rate of 0.6 V/h; the scans were initiated at a potential 0.15 V below the open circuit potential, and terminated after a substantial increase in current density has occurred. The data were stored digitally on magnetic discs; hard copies were then produced, using a scientific plotting program.

Crevice repassivation tests.--The tests were performed for one of the alloys (Code C), using a procedure generally following that of ASTM F746. In this tests an artificial crevice is created on the specimens using a plastic sleeve. The specimen is exposed to 0.9% sodium chloride solution, polarized to a potential of 0.8 V (SCE) to break the passivity and induced an attack; the potential is then dropped to various lower potentials and the current density vs. time response is recorded. the purpose is to determine the potential below which the specimen repassivates, as indicated by current density decreasing with time. The higher this repassivation potential, the more resistant to crevice corrosion is the material. Because of the small diameter of the tested wire specimen a short length (0.25") of PVC tubing, rather than a machined Teflon collar as per ASTM 746, was used to create the artificial crevice.

Results and Discussion

Corrosion potential tests.-- The corrosion potentials for all the tested specimens stabilized in a relatively narrow range of potentials, about -0.05 to +0.05 V (SCE).

Anodic polarization curves.--Anodic polarization for alloy Code A were consistent and showed a region of passivity, ranging from about 0.0 V (SCE) to about 0.8 V (SCE). Thus the measured stabilized corrosion potential was at the lower end of the experimentally observed passivity region, and passivity extended to potential values higher than those expected to be possible in the human body.

The anodic polarization results for specimens Code B showed a short region of passivity, extending only to about -0.05 to +0.15 V (SCE). More tests would be needed to determine the value with greater statistical confidence. It seems clear, however, that the corrosion potential of specimen Code B was close to the high end of the passive region, and that higher rates of dissolution would be expected for specimen Code B than for specimen Code A in the human body environment.

Specimens Code C showed polarization behavior resembling that of Code B, but with a pronounced passivation peak at about -0.1 V (SCE). The region of passivity again was short and the high end was at about -0.15 V (SCE).

Crevice repassivation tests.--Only one of the exploratory tests for material Code A was performed. When the passivity was broken at 0.8 V (SCE) in the presence of an artificial crevice, lowering the potential to a value as low as 0.3 V (SCE) did not result in repassivation. Lowering the potential to 0.15 V (SCE) or lower, on the other hand, caused repassivation of the attacked areas. These preliminary results show that the repassivation potential, under the condition of the ASTM F746 test, probably lies between 0.15 and 0.3 V (SCE) for this material, and seem to indicate some possibility of formation of crevice corrosion cells in the human body environment. Results of these tests, when performed on various alloys, can be used to compare the relative susceptibility to crevice corrosion.

Over... Evaluation ... Conclusions

Results of this preliminary character... of the e... chemical corrosion behavior of the prospective implant alloys, Code A, ... C, show... the corrosion properties can range in a relatively wide range, depending on the ... ct comp...ion and processing of the alloys. The most favorable corrosion behavior was show... by alloy Code A, which exhibited a wide range of passivity. Although the corrosion r... not de... ...ed in this test program, it can be at least predicted that the dissolution rate ... lloy ... stable and not vary widely with changes in the oxidation power of ... ...nment. ... other tested alloys and specimens, on the other hand, showed narrow ranges ... ity, wh... ...d at relatively low potentials. Thus an increase in the oxidation power of ... ...nment ... cause the current density, and the dissolution rate, to increase steeply. ... ...cess... ...lication of the these materials in the human body environment it seems ... ... de... ...the relationship between composition, processing, and the corrosion b...

Quarterly Report

Project: Electrochemical Studies of Implant Materials

REPORT TITLE:

STATIC LEACHING TESTS OF CANDIDATE MATERIALS IN RINGER'S SOLUTION

Submitted to

C.R. Bard, Inc.
1200 Technology Park Drive
P.O. Box 7025
Billerica, MA 01821

by

Miroslav Marek, Ph.D.
Professor
School of Materials Science and Engineering
Georgia Institute of Technology
Atlanta, GA 30332-0245

September 29, 1995

STATIC LEACHING TESTS OF CANDIDATE MATERIALS IN RINGER'S SOLUTION

Objective

The objective of the test was to determine the rates of release of the major alloying from alloys Code D and E in a simulated physiological solution.

Materials and Specimens

The materials and the preparation of the specimens have been described in previously submitted protocols.

Methodology

The methodology is described in detail in a protocol submitted previously. In brief, the specimens were exposed individually in test tubes to Ringer's solution for 2, 4, 6 and 8 weeks at 37°C. Three specimens of each alloy were exposed, and suitable blanks and standard were included. The preparation and use of the blanks and standards have been described. After each exposure period the solution sample from each tube was analyzed for dissolved metal ions. The analytical technique was Anodic Stripping Voltammetry for element (1), and flameless (carbon furnace) Atomic Absorption Spectroscopy for the other elements.

Results

The value of the mass of an element leached out per cm^2, m_i, was calculated as follows:

The increase in concentration Δc_i of the element i in the test tube Δc_i [concentration in ppm or ppb; 1 ppm (μg /mL) = 1000 ppb (ng/mL)]

$$\Delta c_i = c_t - c_o \qquad (1)$$

where c_t is the concentration at the exposure time t, and c_o is the initial concentration in the test tube (1 ppb), was multiplied by the volume of the solution in the test tube V (20 mL) and divided by the surface area of the specimen S_i [cm^2],

2

$$m_i = (\Delta c_i \times V \times K)/S_i \qquad (2)$$

where K is a numerical constant for the unit conversion; $K = 1$ for Δc_i in ppm, $K = 10^{-3}$ for Δc_i in ppb, for m_i in $\mu g/cm^2$.

Figure 1 shows the results for all the elements for alloy Code D, and Figure 2 is a similar plot for alloy Code E.

Conclusions

Both alloys showed a similar trend of faster initial dissolution, followed by stabilization of the dissolution rate at a lower value. Because of the choice of the first exposure period (2 weeks) the measured initial dissolution rate is not necessarily the highest rate at which dissolution occurred shortly after the beginning of the exposure. The observed longer-term dissolution rate, on the other hand, appears to be reliable as a stabilized rate of dissolution.

The results show that the total dissolution rate was higher for alloy Code D than for alloy Code E by a factor of about four initially, and by a factor of about 2.4 when dissolution stabilized.

Figure 1.

Figure 2.

E-18-694

Electrochemical Studies of Implant Materials

Project No. E-18-694

Annual Report 1994

prepared for

USCI Division
C.R. Bard, Inc.
1200 Technology Park Drive
P.O. Box 7025
Billerica, MA 01821

by

Miroslav Marek, Ph.D.
Professor
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Atlanta, GA 30332-0245

January 15, 1995

I. GALVANIC INTERACTIONS BETWEEN IMPLANTED DEVICES MADE OF DIFFERENT ALLOYS

Interaction between dissimilar metals in the human body

When dissimilar metals or alloys come in contact and are exposed to a corrosive environment, galvanic interaction occurs. The interaction is due to redistribution of the anodic (oxidation) and cathodic (reduction) reactions on the metals in contact. After this redistribution a new corrosion potential, common to all the connected surfaces (if electrical resistance effects can be ignored), is established, at which the sum of anodic rates on the different surfaces is equal to the sum of cathodic rates. This potential normally is between the values of the corrosion potential for the different metals, if they were unconnected. Thus the potential of the metal, which individually exhibits a higher potential, would become lower due to the galvanic contact, and *vice versa*. Since the corrosion rate usually increases with increasing potential, the metal exhibiting a higher individual corrosion potential usually corrodes less as a result of the contact, while corrosion of the metal with the lower individual corrosion potential increases due to the contact.

The galvanic interaction requires a metallic contact between the different metals (electrodes). Any contact resistance diminishes the severity of the galvanic interaction, because the corrosion potentials of the different metals are no longer equal, but differ by the IR drop across the resistance.

Galvanic interaction between devices made of alloy A and alloy B in the human body

If a device, made of alloy A, has been implanted, and a new device, made of alloy B, is placed in the vicinity, the possibility of a metallic contact between the devices exists. If a low resistance contact between the devices is established, the two materials would react galvanically. Results of long-term corrosion potential measurements for alloy specimens exposed to a simulated tissue fluid environment have shown that alloy A exhibited consistently a higher corrosion potential than B. Thus the effect of a galvanic interaction would be to lower slightly the corrosion potential of alloy A, and slightly increase the corrosion potential of alloy B.

The effect of the above change on the corrosion potential can be evaluated on the basis of the anodic polarization behavior of the two alloys. Polarization tests have shown that both alloys, when exposed to simulated body fluids, were in a passive state, *i.e.*, covered and protected by a thin oxide film, and the corrosion rate was very low. Above a critical potential (breakdown potential), however, the film breaks down locally and pitting occurs. Thus any lowering of the corrosion potential due to a galvanic contact of alloy A with alloy B would slightly decrease the probability of breakdown and pitting, although it might not prevent it.

For alloy B, the individual corrosion potential also lies in the passive range. A slight increase in the corrosion potential due to a galvanic interaction with alloy A would have a negligible effect on the corrosion rate of alloy B, since the anodic polarization curve is almost flat (*i.e.*, vertical on the graph.

Conclusions

Although direct galvanic measurements have not been performed in this study, the results of corrosion potential and anodic polarization measurements indicate that a galvanic interaction by direct metallic contact between alloy A and alloy B in the human body environment would not cause increased corrosion of either alloy. If the previously implanted device were encapsulated or covered with a layer of cells, the increase in contact resistance would tend to make the corrosion behavior of the devices independent of each other.

II. CORROSION OF A GALVANIC COUPLE OF ALLOY B WITH A NOBLE METAL

1. Anodic polarization measurement

The anodic polarization curve was obtained for the as-received specimen. Compared with the polarization curve for alloy B, the zero current potential of the assembly was substantially higher, which can be attributed to the galvanic effect of the more noble alloy. The behavior above the zero current potential roughly followed the polarization behavior of alloy B. This is expected since the noble alloy probably shows little activity in this potential range, except perhaps at the highest potentials used in the test, so that the behavior is dominated by the alloy B.

2. Corrosion potential vs. time test

The initial corrosion potential of the galvanic couple was close to the redox potential of the solution, which was about +0.35 V (SCE). Since the surface area of the couple is dominated by the large surface area of the noble alloy, the results are consistent with a corrosion potential of a galvanic couple, in which the cathode area is large and the anode is small and has a low corrosion rate. In such a case the potential is determined by the potential of the noble cathode, and the anode has little effect. The drop in the corrosion potential with time, however, seems to indicate that the corrosion rate increased with time. Since it is unlikely that the corrosion rate of the noble alloy substantially increased, it seems that the potential drop was due to activation of the alloy B, perhaps in the form of crevice corrosion, accelerated by the galvanic coupling with the noble alloy. It is thus conceivable that the galvanic coupling caused accelerated attack of alloy B, which in turn resulted in the formation of crevice corrosion conditions. (Crevice corrosion requires some accumulation of dissolved metal ions for generation of acidity

3. Galvanic current vs. time test

In this test the two alloys were separated and immersed in the electrolyte, and connected externally through a zero-shunt ammeter, which measured the galvanic current flowing between the anode and cathode. In this arrangement the connection simulates the galvanic contact, but the insertion of the ammeter allows the current to be measured while both parts of the galvanic couple are at the same potential. The results show that the current initially decreased; this is a normal behavior, related to the growth of the film on the anode as its potential is increased by the galvanic contact. After about 30 hours of exposure the current slowly increased with time. The cause of this increase is not known; there was no intentional crevice, to which the increase could be attributed. It is possible, however, that some crevice condition developed in the region of attachment to the holder. The galvanic current densities generally were low; in the initial time period they were estimated to be about 10-20% of the passive current density for the same exposure time. The galvanic current density at the end of the test was even lower, but the increasing trend is of some concern.

4. Examination following a medium-length exposure

To examine if crevice corrosion might occur, one galvanic assembly was exposed to Ringer's solution at 37°C for 60 hours. Following the exposure the galvanic couple was disassembled and examined in a Scanning Electron Microscope (SEM).

The results of the SEM examination have shown numerous sites of attack, indicating initiation of crevice corrosion. Together with the electrochemical test results, the SEM evidence indicates that the initial high potential, caused by the combination of the noble alloy and alloy B resulted in accelerated dissolution of alloy B. In the crevice between the two parts of the galvanic couple this dissolution apparently caused local chemistry changes, especially acidification, resulting in the initiation of crevice corrosion.

The above galvanic/crevice corrosion attack appears to be caused by the combination of two effects: (1) a galvanic couple consisting of a large area of a noble cathode and a small area anode, which is the most unfavorable condition in galvanic cells, and (2) the crevices formed at the contacts between the parts of the couple. It is quite possible that either of the two effects alone would not cause severe degradation: the galvanic coupling would likely increase the dissolution rate, but the form of dissolution would be uniform and not necessarily very intensive; the crevice condition, without a potential increase by the galvanic coupling would not necessarily cause attack on alloy B, which is quite resistant to crevice corrosion under open circuit conditions

Annual Report

ELECTROCHEMICAL STUDIES OF IMPLANT MATERIALS

By:
Miroslav Marek, Ph.D.
School of Materials Science and Engineering

Under:
AGREEMENT DTD 12/22/93
C.R. Bard, Inc.
1200 Technology Park Drive
P.O. Box 7025
Billerica, MA 01821

Period of Performance:
01/01/95 - 12/31/95

December 30, 1995

TABLE OF CONTENTS

Study I

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Methodology

Two types of electrochemical tests were performed. The first technique essentially follows the procedure described by Postlethwaite, 1981.[1] In this test the specimen is exposed to an electrolyte containing dissolved oxygen, and the electrode potential is measured. The potential is then maintained, using an electronic potentiostat, at the same value (corrosion potential), and the dissolved oxygen is removed by deaeration with pure nitrogen, thus eliminating the cathodic current of oxygen reduction. The controlling current is then equal to the anodic current, which is proportional to the corrosion rate. In this series of tests the current during the measurement period was integrated, and the average current was determined by dividing the integrated current (charge) by the time of the measurement period (usually 1 hour).

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Tests of two specimens have been completed. The data show an increase in polarization resistance with exposure time, consiimplant with the inverse relationship between polarization resistance and corrosion current density.

The polarization resistance R_p is related to the corrosion current density i_{cor} as follows[2]:

$$R_p = B/2.3 \, i_{cor} \qquad (1)$$

where B is a numerical parameter, which is a function of the polarization (Tafel) constants b_a and b_c as follows:

$$B = b_a \, b_c /(b_a + b_c) \qquad (2)$$

When the constants b_a and b_c are not known, as in this case, the parameter B can be estimated, based on the knowledge of usual values of the constants. When the electrode is in an ideally passive state and the current density is totally potential independent, B is equal to b_c. Since both the polarization test data and the polarization resistance data showed nearly constant values for longer exposures, the average current density for all exposures of 17 days and

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To obtain a single elements dissolution rate corresponding to current density, Faraday's law is used[3],

$$m = i \, t \, A/n \, F \tag{3}$$

where m is the reacted (dissolved) mass per unit area, i is current density, t is time, A is atomic weight of the element, n is the change in the oxidation state (ionic charge of the element dissolved), and F is Faraday's constant (96,493 C/equivalent). The dissolution rate[3] of an element

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If the assumption is that the alloying elements dissolve proportionately to their concentration in the alloy, the total charge per unit time (product $i_{avg} \, t$ in equation (3)) must be partitioned. The partitioning coefficient k_i

$$k_i = ((x_i \, n_i/A_i)/(\Sigma (x_i \, n_i/A_i)) \tag{6}$$

---

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5

where x_i is the number of grams of an element in a unit mass of the alloy, and A_i, n_i are the atomic weight and oxidation state, respectively, for each major alloying element. The average daily release rate of an element is then calculated as follows:

$$r_i' = (i_{avg}\, k_i\, A_i\, /\, n_i\, F)\; 8.64E4 \text{ s/day} \quad [\text{g/day}] \tag{7}$$

Study II

PRELIMINARY CHARACTERIZATION OF THE ELECTROCHEMICAL CORROSION BEHAVIOR OF PROSPECTIVE ALLOYS IN RINGER'S SOLUTION

Objective

The objective of the test program was a preliminary evaluation of the corrosion susceptibility and behavior of specimens of three new prospective alloys in a simulated human body environment.

Materials

The specimens included wire specimens of three alloys of similar composition, Coded A, B and C, supplied by C.R. Bard, Inc

Test Program

The test program consisted of limited electrochemical characterization using corrosion potential and potentiodynamic anodic polarization measurements. Exploratory crevice repassivation tests were performed for Code A alloy.

Test specimens

For testing the specimens were in the form of a loop immersed in the solution. The exposed area, determined for each wire size, ranged from 0.85 to 1.5 cm^2.

Test media

For the corrosion potential and anodic polarization tests the specimens were exposed to Ringer's solution adjusted to 7.4, at 37°C. The composition of the solution was as follows:

NaCl	9.0 g/L
CaCl$_2$.2H$_2$O	0.17 g/L
KCl	0.4 g/L
NaHCO$_3$	0.2 g/L

For corrosion potential measurements the solution was saturated with an atmosphere of 6% oxygen, 5% carbon dioxide and balance nitrogen. For the anodic polarization tests the

solution was deaerated using a high purity nitrogen gas. The crevice repassivation tests were performed using 0.9% sodium chloride solution, exposed to air.

Test procedures

Corrosion potential tests.--The specimens were tested in a two-electrode glass cell, jacketed for temperature control by circulation of water from a constant-temperature circulator. The potential was measured with respect to a Saturated Calomel Electrode (SCE). The equipment consisted of an electronic potentiostat controlled by a microprocessor (Model 351, EG&G Princeton Applied Research, Princeton, NJ). The potentials were measured for exposure periods ranging from 24 to 92 hours, starting immediately after filling the cell with the solution.

Anodic polarization tests.--The specimens were tested in a three-electrode glass cell, temperature-controlled at 37°C. A Saturated Calomel Electrode (SCE) with a salt bridge and a Luggin capillary was used as a reference, and a platinum wire as counter-electrode. The equipment consisted of an electronic potentiostat controlled by a microprocessor (Model 351, EG&G Princeton Applied Research, Princeton, NJ). Potentiodynamic polarization curves were recorded at a potential scanning rate of 0.6 V/h; the scans were initiated at a potential 0.15 V below the open circuit potential, and terminated after a substantial increase in current density has occurred. The data were stored digitally on magnetic discs; hard copies were then produced, using a scientific plotting program.

Crevice repassivation tests.--The tests were performed for one of the alloys (Code C), using a procedure generally following that of ASTM F746. In this tests an artificial crevice is created on the specimens using a plastic sleeve. The specimen is exposed to 0.9% sodium chloride solution, polarized to a potential of 0.8 V (SCE) to break the passivity and induced an attack; the potential is then dropped to various lower potentials and the current density vs. time response is recorded. the purpose is to determine the potential, below which the specimen repassivates, as indicated by current density decreasing with time. The higher this repassivation potential, the more resistant to crevice corrosion is the material. Because of the

small diameter of the tested wire specimen a short length (0.25") of PVC material, rather than a machined Teflon collar as per ASTM 746, was used to create the artificial crevice.

Results and Discussion

Corrosion potential tests.-- The corrosion potentials for all the tested specimens stabilized in a relatively narrow range of potentials, about -0.05 to +0.05 V (SCE).

*Anodic polarization curves.--*Anodic polarization for alloy Code A were consiimplant and showed a region of passivity, ranging from about 0.0 V (SCE) to about 0.8 V (SCE). Thus the measured stabilized corrosion potential was at the lower end of the experimentally observed passivity region, and passivity extended to potential values higher than those expected to be possible in the human body.

The anodic polarization results for specimens Code B showed a short region of passivity, extending only to about -0.05 to +0.15 V (SCE). More tests would be needed to determine the value with greater statistical confidence. It seems clear, however, that the corrosion potential of specimen Code B was close to the higher end of the passive region, and that higher rates of dissolution would be expected for specimen Code B than for specimen Code A in the human body environment.

Specimens Code C showed polarization behavior resembling that of Code B, but with a pronounced passivation peak at about -0.4 V (SCE). The region of passivity again was short and the high end was at about -0.15 V (SCE).

*Crevice repassivation tests.--*Only one set of exploratory tests for material Code A was performed. When the passivity was broken at 0.8 V (SCE) in the presence of an artificial crevice, lowering the potential to a value as low as 0.3 V (SCE) did not result in repassivation. Lowering the potential to 0.15 V (SCE) or lower, on the other hand, caused repassivation of the attacked areas. These preliminary results show that the repassivation potential, under the condition of the ASTM F746 test, probably lies between 0.15 and 0.3 V (SCE) for this material, and seem to indicate some possibility of formation of crevice corrosion cells in the

human body environment. Results of these tests, when performed for various alloys, can be used to compare the relative susceptibility to crevice corrosion.

Overall Evaluation and Conclusions

Results of this preliminary characterization of the electrochemical corrosion behavior of the prospective implant alloys, Code A, B, and C, show that the corrosion properties can range in a relatively wide range, depending on the exact composition and processing of the alloys. The most favorable corrosion behavior was shown by alloy Code A, which exhibited a wide range of passivity. Although the corrosion rate was not determined in this test program, it can be at least predicted that the dissolution rate of the this alloy would be stable and not vary widely with changes in the oxidation power of the environment. The other tested alloys and specimens, on the other hand, showed narrow ranges of passivity, which ended at relatively low potentials. Thus an increase in the oxidation power of the environment would cause the current density, and the dissolution rate, to increase steeply. For a successful application of the these materials in the human body environment it seems essential to determine the relationship between composition, processing, and the corrosion behavior.

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Study III

STATIC LEACHING TESTS OF CANDIDATE MATERIALS IN RINGER'S SOLUTION

Objective

The objective of the test was to determine the rates of release of the major alloying from alloys Code D and E in a simulated physiological solution.

Materials and Specimens

The materials and the preparation of the specimens have been described in previously submitted protocols.

Methodology

The methodology is described in detail in a protocol submitted previously. In brief, the specimens were exposed individually in test materials to Ringer's solution for 2, 4, 6 and 8 weeks at 37°C. Three specimens of each alloy were exposed, and suitable blanks and standard were included. The preparation and use of the blanks and standards have been described. After each exposure period the solution sample from each material was analyzed for dissolved metal ions. The analytical technique was Anodic Stripping Voltammetry for element (1), and flameless (carbon furnace) Atomic Absorption Spectroscopy for the other elements.

Results

The value of the mass of an element leached out per cm^2, m_i, was calculated as follows:

The increase in concentration Δc_i of the element i in the test material Δc_i [concentration in ppm or ppb; 1 ppm (μg /mL) = 1000 ppb (ng/mL)]

$$\Delta c_i = c_t - c_o \qquad (1)$$

where c_t is the concentration at the exposure time t, and c_o is the initial concentration in the test material (1 ppb), was multiplied by the volume of the solution in the test material V (20 mL) and divided by the surface area of the specimen S_i [cm^2],

$$m_i = (\Delta c_i \times V \times K)/S_i \qquad (2)$$

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where K is a numerical constant for the unit conversion; $K = 1$ for Δc_i in ppm, $K = 10^{-3}$ for Δc_i in ppb, for m_i in $\mu g/cm^2$.

Figure 1 shows the results for all the elements for alloy Code D, and Figure 2 is a similar plot for alloy Code E.

Conclusions

Both alloys showed a similar trend of faster initial dissolution, followed by stabilization of the dissolution rate at a lower value. Because of the choice of the first exposure period (2 weeks) the measured initial dissolution rate is not necessarily the highest rate at which dissolution occurred shortly after the beginning of the exposure. The observed longer-term dissolution rate, on the other hand, appears to be reliable as a stabilized rate of dissolution.

The results show that the total dissolution rate was higher for alloy Code D than for alloy Code E by a factor of about four initially, and by a factor of about 2.4 when dissolution stabilized.

Fig. 1

Fig. 2

Study IV

CORROSION BEHAVIOR OF IMPLANTS
IN RINGER'S SOLUTION

Objective

The objective of the test program was to characterize the corrosion behavior of raw material and implants under conditions simulating the environment of the implants in the human body.

Materials and Implants

The following materials and implants were received from C.R. Bard, Inc. for testing:

1. Raw material

2. Implants, Type A

3. Implants, Type B

Methodology

The battery of tests used in this test program for evaluation of the corrosion behavior and corrosion susceptibility of the products included electrochemical tests and nickel leaching tests. The electrochemical test program consisted of corrosion potential and anodic polarization measurements to characterize the general corrosion behavior, and long-term corrosion rate measurements. The leaching tests were designed to measure the rate of nickel dissolution

The purpose of the electrochemical evaluation is described in the previously submitted Protocols.

In the leaching tests included in this Test Program the amounts of nickel leached out during individual 24-hour periods were determined. The test specimens were exposed to the Ringer's solution for a total period of nine weeks; however, a fresh solution was used at specific exposure times and analyzed at the end of each 24-hour test period. This method prevented excessive accumulation of the metal ions in the solution sample, which would have reduced the driving force for dissolution. This test thus simulated the conditions of exposure in the blood vessels.

Results

A. Potentiodynamic Anodic Polarization Curves for Raw Material

The polarization curves have been overlayed in Fig. 1, which shows the data for results for two specimens in the as received conditions. The polarization curves show some passivity, but an early passivity breakdown. The breakdown potential was about -0.1 V (SCE) for all three specimens, followed by a sharp increase in the corrosion current density at higher potentials. Short-term corrosion potential measurements showed the corrosion potential (in the aerated solution) to be close to the breakdown poential, *i.e.*, about -0.1 V (SCE).

B. Potentiodynamic Anodic Polarization Curves for Implants

The results of the polarization measurements are shown in Fig. 2 and 3 for Type A and Type B implants, respectively. The general characteristic of the polarization curves were similar to those for the raw material, i.e., a short region of passivity, and a passivity breakdown above a critical potential. The critical potential ranged from about -0.1 V (SCE) to 0.0 V (SCE). The plots illustrate that the implants exhibited a slightly better polarization behavior then the raw material, i.e., a more positive breakdown potential.

C. Corrosion Potential Results for Implants

The long-term corrosion potential data have been plotted in Fig. 4 for both types of implants. The corrosion potential variation was similar for the two types of implant. The corrosion potentials ranged from -0.186 to -0.044 V (SCE).

D. Long-term Corrosion Rate Results for Implants

The long-term corrosion rate test data have been plotted in Fig. 5.

E. Nickel Leaching Test Results for Implants

The average values of the nickel leaching rate have been plotted in Figs. 6 and 7.

Discussion

Results of the electrochemical measurements of both the raw material and the implants show that the products are passive in Ringer's solution, but that much faster corrosion would, occur with only a slight increase in the corrosion potential, i.e., for a slightly more oxidizing environment than the Ringer's solution. The theoretical maximum of the corrosion potential is the equilibrium potential for the reaction of oxygen, which serves as the major cathodic reactant. Unless there is a stronger oxidant present than the dissolved oxygen, the corrosion potential can only approach, and cannot reach the equilibrium potential of this reaction. A practical maximum if the potential of a non-dissolving electrode; platinum is commonly used for this determination, and the potential is called "redox potential" or ORP (oxidation-reduction potential).

A comparison of the results for the raw material and the implants has shown that the implants exhibited a slightly better corrosion behavior with respect to the raw material, indicating that the surface finish can be effective in improving the corrosion resistance.

Results of the long-term corrosion rate measurements (Fig. 5) and the nickel leaching rate data (Figs. 6 and 7) show that the corrosion rate decreased substantially with the exposure time. This decrease may be attributed to a growth of a protective oxide film or depletion of the surface in nickel, or a combination of both effects.

Conclusions

The test data and their analysis show that the products in the current form exhibit moderate corrosion resistance, but little safety margin for environments with different oxidation powers. The goal should be to extend the region of low corrosion rate to a much higher potential, preferably to the potential of the platinum electrode (redox potential).

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Final Report

ELECTROCHEMICAL STUDIES OF IMPLANT MATERIALS

By:
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PART I

1994-1995

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Study I

LONG-TERM CORROSION RATE OF PROSPECTIVE IMPLANT ALLOYS IN RINGER'S SOLUTION

Objective and Materials

Long-term electrochemical corrosion tests two prospective implant alloys have been performed. For the corrosion tests the wire specimens were exposed to Ringer's solution, saturated with an atmosphere of 6% oxygen, 5% carbon dioxide and balance nitrogen, at 37°C. The pH of the solution was adjusted at 7.4.

Methodology

Two types of electrochemical tests were performed. The first technique essentially follows the procedure described by Postlethwaite, 1981.[1] In this test the specimen is exposed to an electrolyte containing dissolved oxygen, and the electrode potential is measured. The potential is then maintained, using an electronic potentiostat, at the same value (corrosion potential), and the dissolved oxygen is removed by deaeration with pure nitrogen, thus eliminating the cathodic current of oxygen reduction. The controlling current is then equal to the anodic current, which is proportional to the corrosion rate. In this series of tests the current during the measurement period was integrated, and the average current was determined by dividing the integrated current (charge) by the time of the measurement period (usually 1 hour).

The second test methodology was the measurement of the polarization resistance, which is inversely proportional to the corrosion rate. The measurements were performed using the technique of Electrochemical Impedance Spectroscopy (EIS). Since the results do not provide directly the corrosion current density, and the calculation of the corrosion rate requires the knowledge of the Tafel constants, the corrosion rate results were obtained for several assumed values of Tafel constants in the range commonly observed, and also compared with the polarization results.

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[1] J. Postlethwaite, "Direct Measurement of the Corrosion Current for Oxygen-Reduction Corrosion," in *Electrochemical Corrosion Testing*, ASTM STP 727, F. Mansfeld and U. Bertocci, Eds., ASTM, 1981, pp. 290-302.

Results

A. Polarization current density measurements

Two long term polarization tests of each material have been performed. Both materials showed a sharp drop in the corrosion current density from the initial values, and stabilization at a nearly constant current density at longer exposures. The mean current densities after one day exposures were on the order of 10^{-8} A/cm^2. The average current densities calculated for all exposures of 17 days and longer, when the current density was relatively stable, were in the range of 2 to 5×10^{-9} A/cm^2.

B. Polarization resistant measurements by EIS

Tests of two specimens have been completed. The data show an increase in polarization resistance with exposure time, consiimplant with the inverse relationship between polarization resistance and corrosion current density.

The polarization resistance R_p is related to the corrosion current density i_{cor} as follows[2]:

$$R_p = B/2.3 \, i_{cor} \tag{1}$$

where B is a numerical parameter, which is a function of the polarization (Tafel) constants b_a and b_c as follows:

$$B = b_a \, b_c / (b_a + b_c) \tag{2}$$

When the constants b_a and b_c are not known, as in this case, the parameter B can be estimated, based on the knowledge of usual values of the constants. When the electrode is in an ideally passive state and the current density is totally potential independent, B is equal to b_c. Since both the polarization test data and the polarization resistance data showed nearly constant values for longer exposures, the average current density for all exposures of 17 days and

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[2] J.C. Scully, *The Fundamentals of Corrosion*, 2nd ed., Pergamon Press, 1975, p. 86.

longer, when the current density was relatively stable, was then used to calculate the parameter B.

Metal ion dissolution

The electrochemical tests do not provide means for identifying the dissolving species or their distribution. One possible assumption is that the elements dissolve in the proportion of their concentration in the alloy. If one element is considered critical, a worst case assumption is that the dissolution of this element is responsible for all the measured corrosion current density.

To obtain a single elements dissolution rate corresponding to current density, Faraday's law is used[3],

$$m = i\, t\, A/n\, F \tag{3}$$

where m is the reacted (dissolved) mass per unit area, i is current density, t is time, A is atomic weight of the element, n is the change in the oxidation state (ionic charge of the element dissolved), and F is Faraday's constant (96,493 C/equivalent). The dissolution rate[3] of an element

$$r_i = m/t = i\, A_i/n_i\, F \tag{4}$$

If the assumption is that the alloying elements dissolve proportionately to their concentration in the alloy, the total charge per unit time (product $i_{avg}\, t$ in equation (3)) must be partitioned. The partitioning coefficient k_i

$$k_i = ((x_i\, n_i/A_i)/(\Sigma\, (x_i\, n_i/A_i)) \tag{6}$$

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[3] D.A. Jones, *Principles and Prevention of Corrosion*, Maxmillan Publishing Co., 1992, p.75.

where x_i is the number of grams of an element in a unit mass of the alloy, and A_i, n_i are the atomic weight and oxidation state, respectively, for each major alloying element. The average daily release rate of an element is then calculated as follows:

$$r_i{}' = (i_{avg} \, k_i \, A_i \, / \, n_i \, \mathbf{F}) \; 8.64E4 \text{ s/day} \quad [\text{g/day}] \tag{7}$$

Study II

PRELIMINARY CHARACTERIZATION OF THE ELECTROCHEMICAL CORROSION BEHAVIOR OF PROSPECTIVE ALLOYS IN RINGER'S SOLUTION

Objective

The objective of the test program was a preliminary evaluation of the corrosion susceptibility and behavior of specimens of three new prospective alloys in a simulated human body environment.

Materials

The specimens included wire specimens of three alloys of similar composition, Coded A, B and C, supplied by C.R. Bard, Inc

Test Program

The test program consisted of limited electrochemical characterization using corrosion potential and potentiodynamic anodic polarization measurements. Exploratory crevice repassivation tests were performed for Code A alloy.

Test specimens

For testing the specimens were in the form of a loop immersed in the solution. The exposed area, determined for each wire size, ranged from 0.85 to 1.5 cm^2.

Test media

For the corrosion potential and anodic polarization tests the specimens were exposed to Ringer's solution adjusted to 7.4, at 37°C. The composition of the solution was as follows:

NaCl	9.0 g/L
$CaCl_2.2H_2O$	0.17 g/L
KCl	0.4 g/L
$NaHCO_3$	0.2 g/L

For corrosion potential measurements the solution was saturated with an atmosphere of 6% oxygen, 5% carbon dioxide and balance nitrogen. For the anodic polarization tests the

solution was deaerated using a high purity nitrogen gas. The crevice repassivation tests were performed using 0.9% sodium chloride solution, exposed to air.

Test procedures

Corrosion potential tests.--The specimens were tested in a two-electrode glass cell, jacketed for temperature control by circulation of water from a constant-temperature circulator. The potential was measured with respect to a Saturated Calomel Electrode (SCE). The equipment consisted of an electronic potentiostat controlled by a microprocessor (Model 351, EG&G Princeton Applied Research, Princeton, NJ). The potentials were measured for exposure periods ranging from 24 to 92 hours, starting immediately after filling the cell with the solution.

Anodic polarization tests.--The specimens were tested in a three-electrode glass cell, temperature-controlled at 37°C. A Saturated Calomel Electrode (SCE) with a salt bridge and a Luggin capillary was used as a reference, and a platinum wire as counter-electrode. The equipment consisted of an electronic potentiostat controlled by a microprocessor (Model 351, EG&G Princeton Applied Research, Princeton, NJ). Potentiodynamic polarization curves were recorded at a potential scanning rate of 0.6 V/h; the scans were initiated at a potential 0.15 V below the open circuit potential, and terminated after a substantial increase in current density has occurred. The data were stored digitally on magnetic discs; hard copies were then produced, using a scientific plotting program.

Crevice repassivation tests.--The tests were performed for one of the alloys (Code C), using a procedure generally following that of ASTM F746. In this tests an artificial crevice is created on the specimens using a plastic sleeve. The specimen is exposed to 0.9% sodium chloride solution, polarized to a potential of 0.8 V (SCE) to break the passivity and induced an attack; the potential is then dropped to various lower potentials and the current density vs. time response is recorded. the purpose is to determine the potential, below which the specimen repassivates, as indicated by current density decreasing with time. The higher this repassivation potential, the more resistant to crevice corrosion is the material. Because of the

small diameter of the tested wire specimen a short length (0.25") of PVC material, rather than a machined Teflon collar as per ASTM 746, was used to create the artificial crevice.

Results and Discussion

Corrosion potential tests.-- The corrosion potentials for all the tested specimens stabilized in a relatively narrow range of potentials, about -0.05 to +0.05 V (SCE).

Anodic polarization curves.--Anodic polarization for alloy Code A were consiimplant and showed a region of passivity, ranging from about 0.0 V (SCE) to about 0.8 V (SCE). Thus the measured stabilized corrosion potential was at the lower end of the experimentally observed passivity region, and passivity extended to potential values higher than those expected to be possible in the human body.

The anodic polarization results for specimens Code B showed a short region of passivity, extending only to about -0.05 to +0.15 V (SCE). More tests would be needed to determine the value with greater statistical confidence. It seems clear, however, that the corrosion potential of specimen Code B was close to the higher end of the passive region, and that higher rates of dissolution would be expected for specimen Code B than for specimen Code A in the human body environment.

Specimens Code C showed polarization behavior resembling that of Code B, but with a pronounced passivation peak at about -0.4 V (SCE). The region of passivity again was short and the high end was at about -0.15 V (SCE).

Crevice repassivation tests.--Only one set of exploratory tests for material Code A was performed. When the passivity was broken at 0.8 V (SCE) in the presence of an artificial crevice, lowering the potential to a value as low as 0.3 V (SCE) did not result in repassivation. Lowering the potential to 0.15 V (SCE) or lower, on the other hand, caused repassivation of the attacked areas. These preliminary results show that the repassivation potential, under the condition of the ASTM F746 test, probably lies between 0.15 and 0.3 V (SCE) for this material, and seem to indicate some possibility of formation of crevice corrosion cells in the

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human body environment. Results of these tests, when performed for various alloys, can be used to compare the relative susceptibility to crevice corrosion.

Overall Evaluation and Conclusions

Results of this preliminary characterization of the electrochemical corrosion behavior of the prospective implant alloys, Code A, B, and C, show that the corrosion properties can range in a relatively wide range, depending on the exact composition and processing of the alloys. The most favorable corrosion behavior was shown by alloy Code A, which exhibited a wide range of passivity. Although the corrosion rate was not determined in this test program, it can be at least predicted that the dissolution rate of the this alloy would be stable and not vary widely with changes in the oxidation power of the environment. The other tested alloys and specimens, on the other hand, showed narrow ranges of passivity, which ended at relatively low potentials. Thus an increase in the oxidation power of the environment would cause the current density, and the dissolution rate, to increase steeply. For a successful application of the these materials in the human body environment it seems essential to determine the relationship between composition, processing, and the corrosion behavior.

Study III

STATIC LEACHING TESTS OF CANDIDATE MATERIALS IN RINGER'S SOLUTION

Objective

The objective of the test was to determine the rates of release of the major alloying from alloys Code D and E in a simulated physiological solution.

Materials and Specimens

The materials and the preparation of the specimens have been described in previously submitted protocols.

Methodology

The methodology is described in detail in a protocol submitted previously. In brief, the specimens were exposed individually in test materials to Ringer's solution for 2, 4, 6 and 8 weeks at 37°C. Three specimens of each alloy were exposed, and suitable blanks and standard were included. The preparation and use of the blanks and standards have been described. After each exposure period the solution sample from each material was analyzed for dissolved metal ions. The analytical technique was Anodic Stripping Voltammetry for element (1), and flameless (carbon furnace) Atomic Absorption Spectroscopy for the other elements.

Results

The value of the mass of an element leached out per cm^2, m_i, was calculated as follows:

The increase in concentration Δc_i of the element i in the test material Δc_i [concentration in ppm or ppb; 1 ppm (μg /mL) = 1000 ppb (ng/mL)]

$$\Delta c_i = c_t - c_o \qquad (1)$$

where c_t is the concentration at the exposure time t, and c_o is the initial concentration in the test material (1 ppb), was multiplied by the volume of the solution in the test material V (20 mL) and divided by the surface area of the specimen S_i [cm^2],

$$m_i = (\Delta c_i \times V \times K)/S_i \qquad (2)$$

13

where K is a numerical constant for the unit conversion; $K = 1$ for Δc_i in ppm, $K = 10^{-3}$ for Δc_i in ppb, for m_i in $\mu g/cm^2$.

Figure 1 shows the results for all the elements for alloy Code D, and Figure 2 is a similar plot for alloy Code E.

Conclusions

Both alloys showed a similar trend of faster initial dissolution, followed by stabilization of the dissolution rate at a lower value. Because of the choice of the first exposure period (2 weeks) the measured initial dissolution rate is not necessarily the highest rate at which dissolution occurred shortly after the beginning of the exposure. The observed longer-term dissolution rate, on the other hand, appears to be reliable as a stabilized rate of dissolution.

The results show that the total dissolution rate was higher for alloy Code D than for alloy Code E by a factor of about four initially, and by a factor of about 2.4 when dissolution stabilized.

Fig. 1

Fig. 2

Study IV

CORROSION BEHAVIOR OF IMPLANTS
IN RINGER'S SOLUTION

Objective

The objective of the test program was to characterize the corrosion behavior of raw material and implants under conditions simulating the environment of the implants in the human body.

Materials and Implants

The following materials and implants were received from C.R. Bard, Inc. for testing:

1. Raw material

2. Implants, Type A

. 3. Implants, Type B

Methodology

The battery of tests used in this test program for evaluation of the corrosion behavior and corrosion susceptibility of the products included electrochemical tests and nickel leaching tests. The electrochemical test program consisted of corrosion potential and anodic polarization measurements to characterize the general corrosion behavior, and long-term corrosion rate measurements. The leaching tests were designed to measure the rate of nickel dissolution

The purpose of the electrochemical evaluation is described in the previously submitted Protocols.

In the leaching tests included in this Test Program the amounts of nickel leached out during individual 24-hour periods were determined. The test specimens were exposed to the Ringer's solution for a total period of nine weeks; however, a fresh solution was used at specific exposure times and analyzed at the end of each 24-hour test period. This method prevented excessive accumulation of the metal ions in the solution sample, which would have reduced the driving force for dissolution. This test thus simulated the conditions of exposure in the blood vessels.

Results

A. Potentiodynamic Anodic Polarization Curves for Raw Material

The polarization curves have been overlayed in Fig. 1, which shows the data for results for two specimens in the as received conditions. The polarization curves show some passivity, but an early passivity breakdown. The breakdown potential was about -0.1 V (SCE) for all three specimens, followed by a sharp increase in the corrosion current density at higher potentials. Short-term corrosion potential measurements showed the corrosion potential (in the aerated solution) to be close to the breakdown poential, *i.e.*, about -0.1 V (SCE).

B. Potentiodynamic Anodic Polarization Curves for Implants

The results of the polarization measurements are shown in Fig. 2 and 3 for Type A and Type B implants, respectively. The general characteristic of the polarization curves were similar to those for the raw material, i.e., a short region of passivity, and a passivity breakdown above a critical potential. The critical potential ranged from about -0.1 V (SCE) to 0.0 V (SCE). The plots illustrate that the implants exhibited a slightly better polarization behavior then the raw material, i.e., a more positive breakdown potential.

C. Corrosion Potential Results for Implants

The long-term corrosion potential data have been plotted in Fig. 4 for both types of implants. The corrosion potential variation was similar for the two types of implant. The corrosion potentials ranged from -0.186 to -0.044 V (SCE).

D. Long-term Corrosion Rate Results for Implants

The long-term corrosion rate test data have been plotted in Fig. 5.

E. Nickel Leaching Test Results for Implants

The average values of the nickel leaching rate have been plotted in Figs. 6 and 7.

Discussion

Results of the electrochemical measurements of both the raw material and the implants show that the products are passive in Ringer's solution, but that much faster corrosion would, occur with only a slight increase in the corrosion potential, i.e., for a slightly more oxidizing environment than the Ringer's solution. The theoretical maximum of the corrosion potential is the equilibrium potential for the reaction of oxygen, which serves as the major cathodic reactant. Unless there is a stronger oxidant present than the dissolved oxygen, the corrosion potential can only approach, and cannot reach the equilibrium potential of this reaction. A practical maximum if the potential of a non-dissolving electrode; platinum is commonly used for this determination, and the potential is called "redox potential" or ORP (oxidation-reduction potential).

A comparison of the results for the raw material and the implants has shown that the implants exhibited a slightly better corrosion behavior with respect to the raw material, indicating that the surface finish can be effective in improving the corrosion resistance.

Results of the long-term corrosion rate measurements (Fig. 5) and the nickel leaching rate data (Figs. 6 and 7) show that the corrosion rate decreased substantially with the exposure time. This decrease may be attributed to a growth of a protective oxide film or depletion of the surface in nickel, or a combination of both effects.

Conclusions

The test data and their analysis show that the products in the current form exhibit moderate corrosion resistance, but little safety margin for environments with different oxidation powers. The goal should be to extend the region of low corrosion rate to a much higher potential, preferably to the potential of the platinum electrode (redox potential).
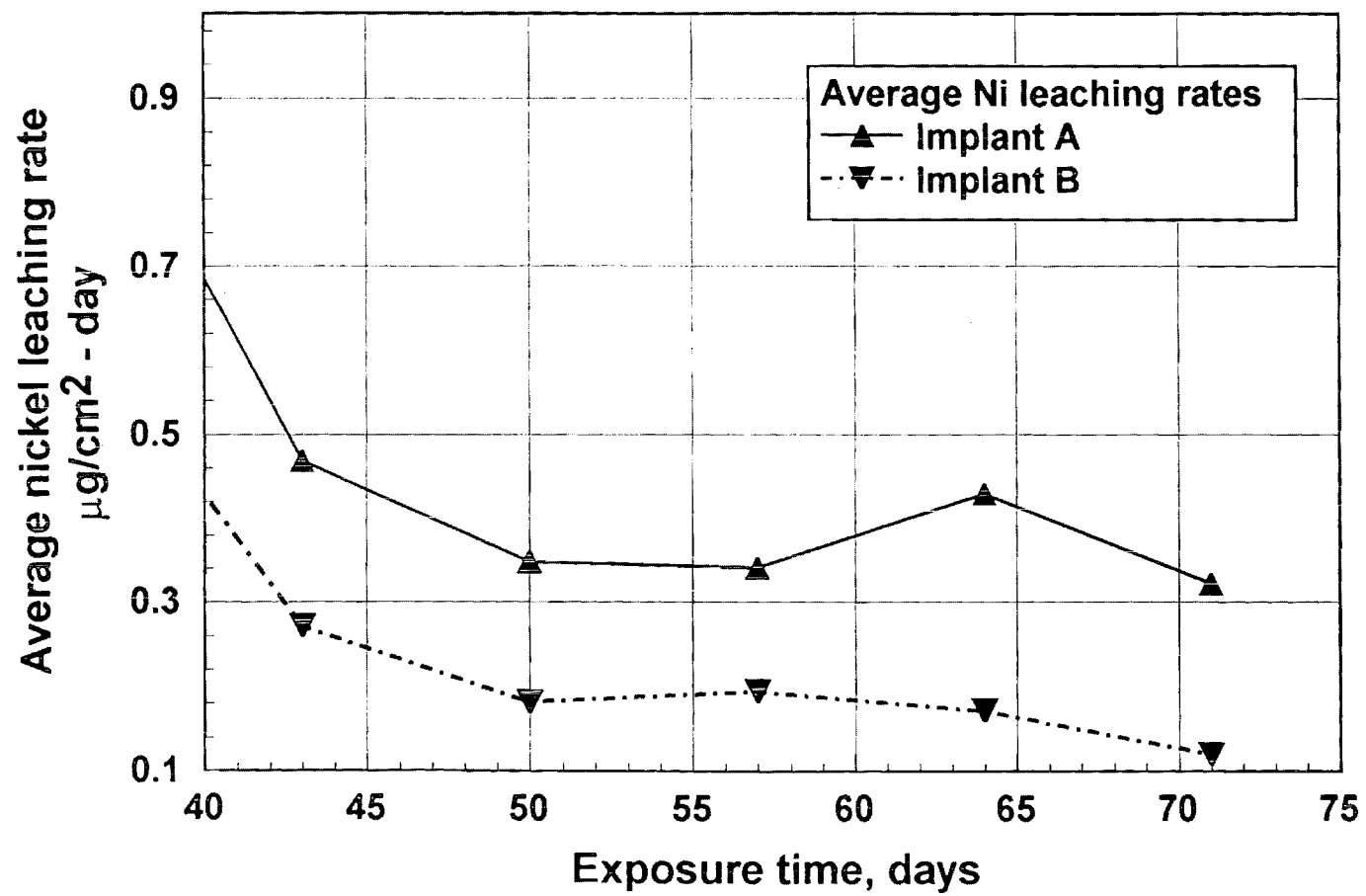
Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

PART II

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CORROSION BEHAVIOR OF BIOMEDICAL DEVICES IN 10% NEUTRAL BUFFERED FORMALIN SOLUTION AND GERMAN FORMOL

Objective

The objective of the test program was to characterize the corrosion behavior of biomedical devices in a storage solution used for explants.

Materials and Devices

The following materials were received from C.R. Bard, Inc. for testing:

3ea Biomedical devices

10% Neutral Buffered Formalin Solution (Sigma Diagnostics, St. Louis, MO 63178, Cat. No. HT50-1-128, Lot 065H4383)

Solution identified by the sponsor verbally as a storage medium received from Germany. The solution is identified further in this report as "German Formol."

Methodology

Each biomedical device was cut in two equal lengths and prepared as an electrode by attaching a piece of stainless steel hypodermic tubing by spot welding to allow connection to the test equipment. The stainless steel tubing was inserted in a glass tube and the joint was insulated using metallographic epoxy resin.

The solutions were used as received, at room temperature, and were saturated with air. The pH of both solutions was measured.

The electrochemical test program consisted of corrosion potential and anodic polarization measurements to characterize the general corrosion behavior. The tests were performed using a standard 3-electrode glass corrosion cell, with platinum wire as a counter-electrode. The potentials were measured with respect to a standard Saturated Calomel Electrode (SCE). Three replicate tests were performed using the 10% Neutral Buffered Formalin Solution, and two replicate tests were performed using German Formol.

All tests were performed at room temperature and using a solution saturated with air. The air saturation provides the worst case condition in the corrosion potential measurements, because it maximizes the oxidation power of the solution while maintaining relevant exposure conditions. Air saturation also was used for the potentiodynamic polarization measurements

instead of the more common solution deaeration. Since the exact chemistry (buffer) of the commercial solution was not known the use of air as atmosphere avoided a possible change of pH, which might result from deaeration.

Results

The pH of the 10% Neutral Buffered Formalin Solution was pH 7.3. The pH of the German Formol was pH 3.95, indicating that the solution was not buffered.

The results of the corrosion potential vs. time measurements are shown in Fig. 1. The test exposure was 15 hours for two specimens and 50 hours for the third specimen in the 10% Neutral Buffered Formalin Solution, and 16 hours for the two specimens in German Formol. In all tests the potential increased with time, but the rate of increase was very slow after 15 hours of exposure. For the specimens in 10% Neutral Buffered Formalin Solution the mean potential was -0.103 V, SCE (S.D. < 1 mV) after 15 hours; after 50 hours of exposure the potential of the third specimen was -0.081 V (SCE). For the two specimens the mean potential between 14 and 15 hours of exposure was +0.053 V (SCE).

The potentiodynamic anodic polarization curves are shown in Fig. 2. Since the solution was not deaerated the zero current potentials were close to the corrosion potentials. The polarization behavior was similar for specimens in either solution. All specimens exhibited a wide range of passivity above the zero current potential. At potentials higher than 0.8 V (SCE) for specimens in 10% Neutral Buffered Formalin Solution and above about 1.0 V (SCE) for specimens in German Formol there was an increase in current density indicating an onset of one or more anodic reactions.

Discussion

The results showed a similar behavior in both solutions in spite of the difference in the pH. Since both solutions are assumed to be solutions of formaldehyde in water, the only difference appears to be that the solution supplied by Sigma was buffered to a near-neutral value, while the solution received from Germany has not been buffered and therefore was rather acidic. The open circuit corrosion potential difference and the difference in the potential of current

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increase were consistent with the difference in the pH values. There was no breakdown of passivity in either solution, apparently because of the lack of aggressive ions in the solutions. No clear difference in the current density in the passive state could be determined due to the small number of replicate tests.

The potential above which a current density increase was observed on the polarization curves was higher than the theoretical maximum for the corrosion potential (about 0.5 V (SCE), the oxygen redox potential). The most likely cause of the current increase was electrolysis of water, i.e., anodic evolution of oxygen.

Conclusions

Test results of the electrochemical tests have shown that biomedical devices exposed to either a 10% buffered formalin solution, or a storage solution received from Germany ("German Formol"), at room temperature and in the presence of air, were in the state of passivity. The results have not shown any indication of susceptibility to a passivity breakdown, which would result in pitting in the above solutions.
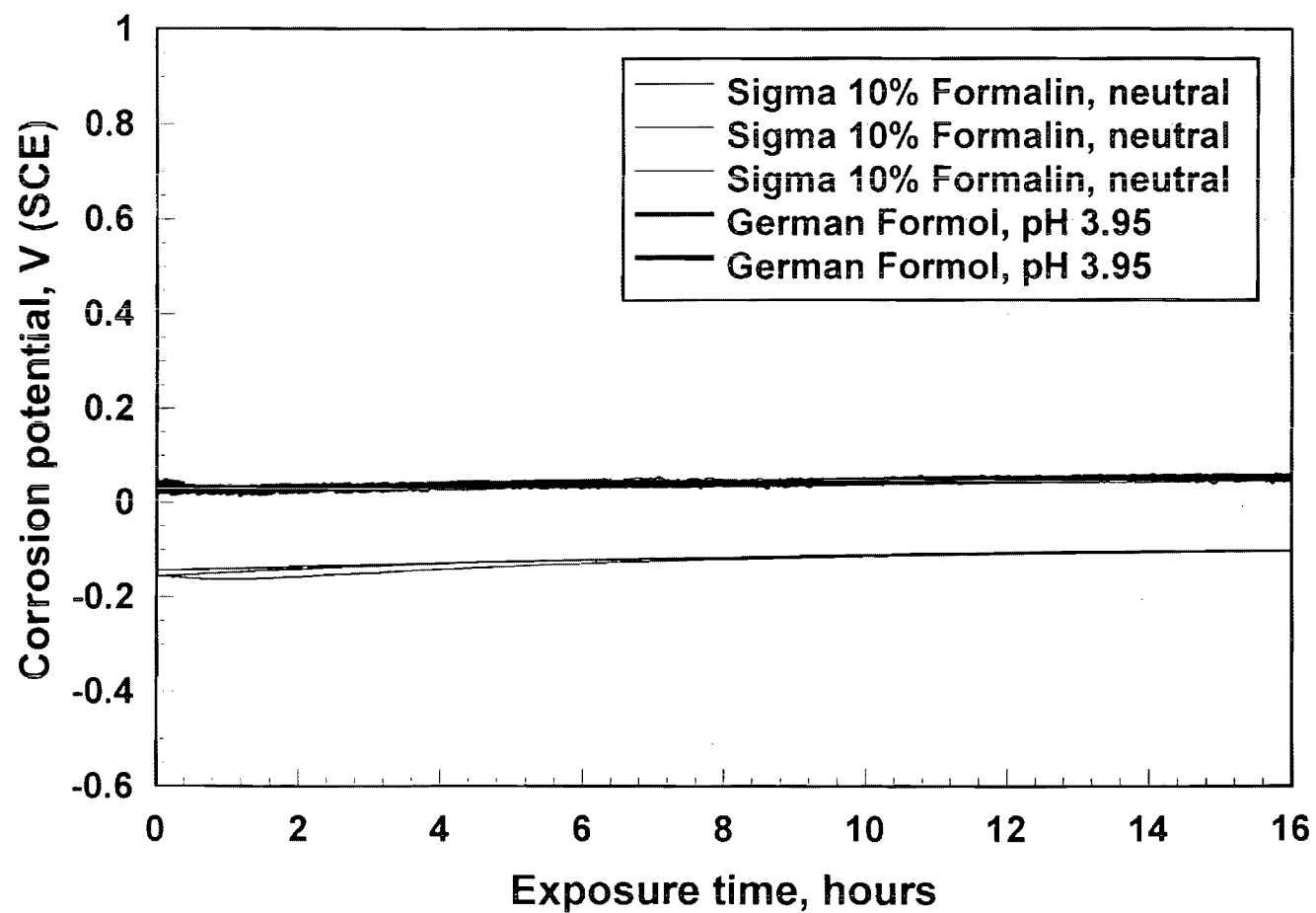
Study I - Fig. 1
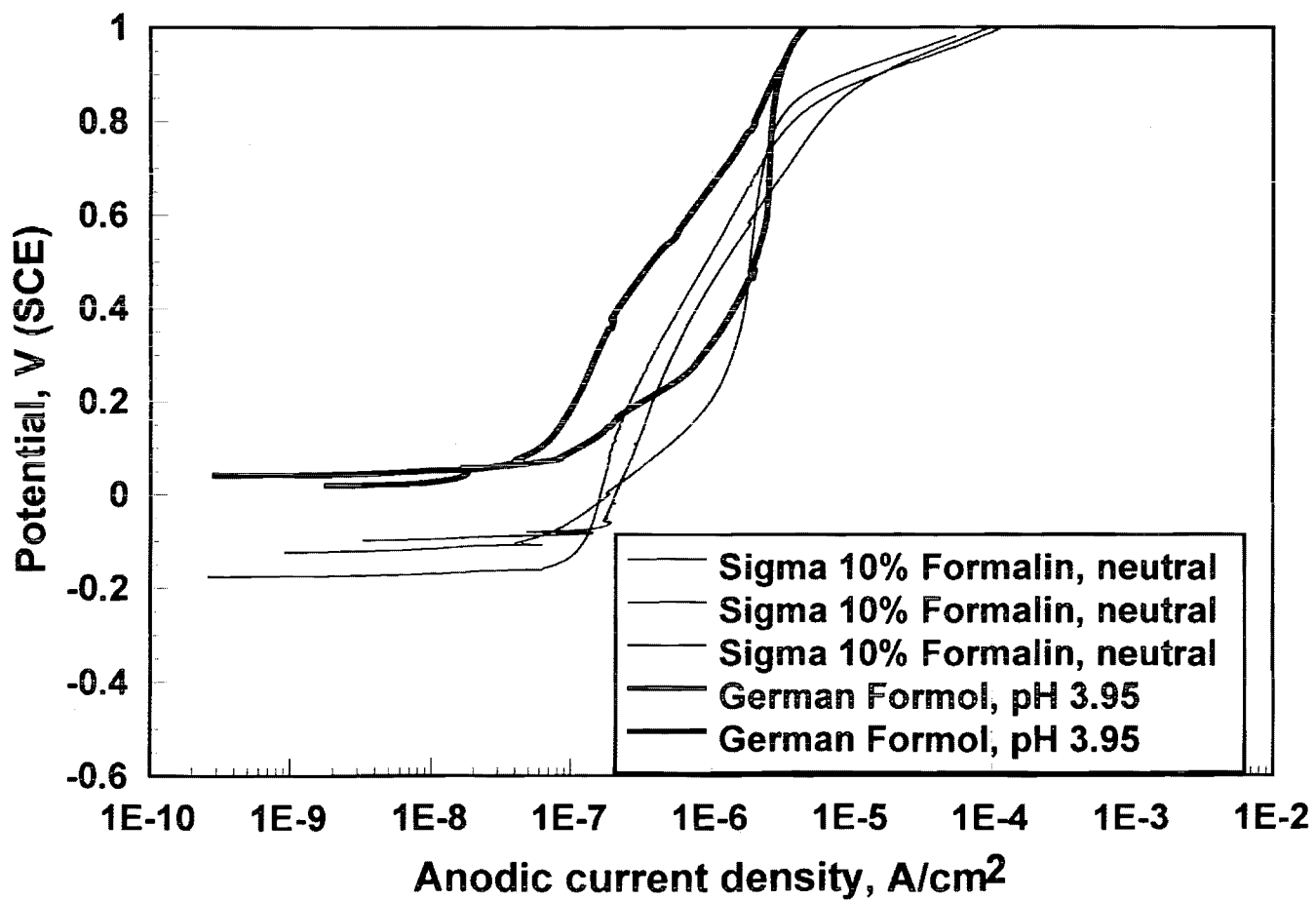
Study I - Fig. 2

Study II

CORROSION POTENTIAL AND POLARIZATION BEHAVIOR OF
A SALT BATH-TREATED BIOMEDICAL DEVICE

Specimens

The biomedical device received from C.R. Bard, Inc. for testing was identified as biomedical device, which had been subjected to heat treatment using a salt bath process. The as-received biomedical device was cut in two half-length specimens, which were prepared as electrodes (Samples A and B).

Methodology

Both specimens were subjected to standard corrosion potential *vs.* time and potentiodynamic anodic polarization measurements. The procedures had been described in previously submitted protocols. The electrolyte was Ringer's solution, pH 7.4 at 37°C. For the corrosion potential measurements the electrolyte was saturated with a gas mixture containing 10% oxygen, 5% carbon dioxide, and balance nitrogen. For the potentiodynamic anodic polarization measurements the solution was deaerated using a gas mixture containing 5% carbon dioxide in oxygen-free nitrogen.

Results and Interpretation

The corrosion potential *vs.* time curves for both Samples A and B are shown in Fig. 1 Both specimens showed very similar corrosion potentials, featuring a very slight tendency to increase (become less negative) with time. At the end of the test exposure (16 h) the corrosion potentials were -0.212 and -0.197 V (SCE). These corrosion potential maxima were thus more negative by about 80 mV than the average corrosion potential maxima for the biomedical devices tested earlier[1].

The anodic polarization curves for Samples A and B are shown in Fig. 2. Both specimens showed passivation followed by a breakdown of passivity. The breakdown potentials were 0.090 V (SCE) and 0.081 V (SCE) for Samples A and B, respectively. This can be compared with the mean breakdown potential of 0.030 V (SCE) (S.D. 0.040, range -0.045 to 0.096 V, SCE) for the biomedical devices tested previously[1]. This comparison shows that while the

breakdown potentials for the two tested specimens were near the upper limit of the previously observed range, they were not significantly different from the average.

Fig. 2 shows that the two samples, prepared from the same biomedical device, showed substantially different behavior at potentials below the breakdown. Specimen B exhibited a typical polarization curve for a passivating electrode, with a region of passivity in which the current density was nearly potential independent. Sample A, on the other hand, exhibited a substantial current peak below the breakdown potential, with a peak current at about -0.05 V (SCE). Considering the difference in the results for the two halves of the same biomedical device it appears that the current peak was caused by some contamination of the surface, possibly in the salt bath. This interpretation is supported by the results of the successive scans (Fig. 3), which shows a smaller peak when the potentiodynamic scan was repeated, presumably because some of the contamination has been removed by the dissolution during the first scan.

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[1] M. Marek: Corrosion behavior of Biomedical Products in Ringer's Solution. First Addendum. Test Report submitted to C.R. Bard, Inc., June 18, 1996.
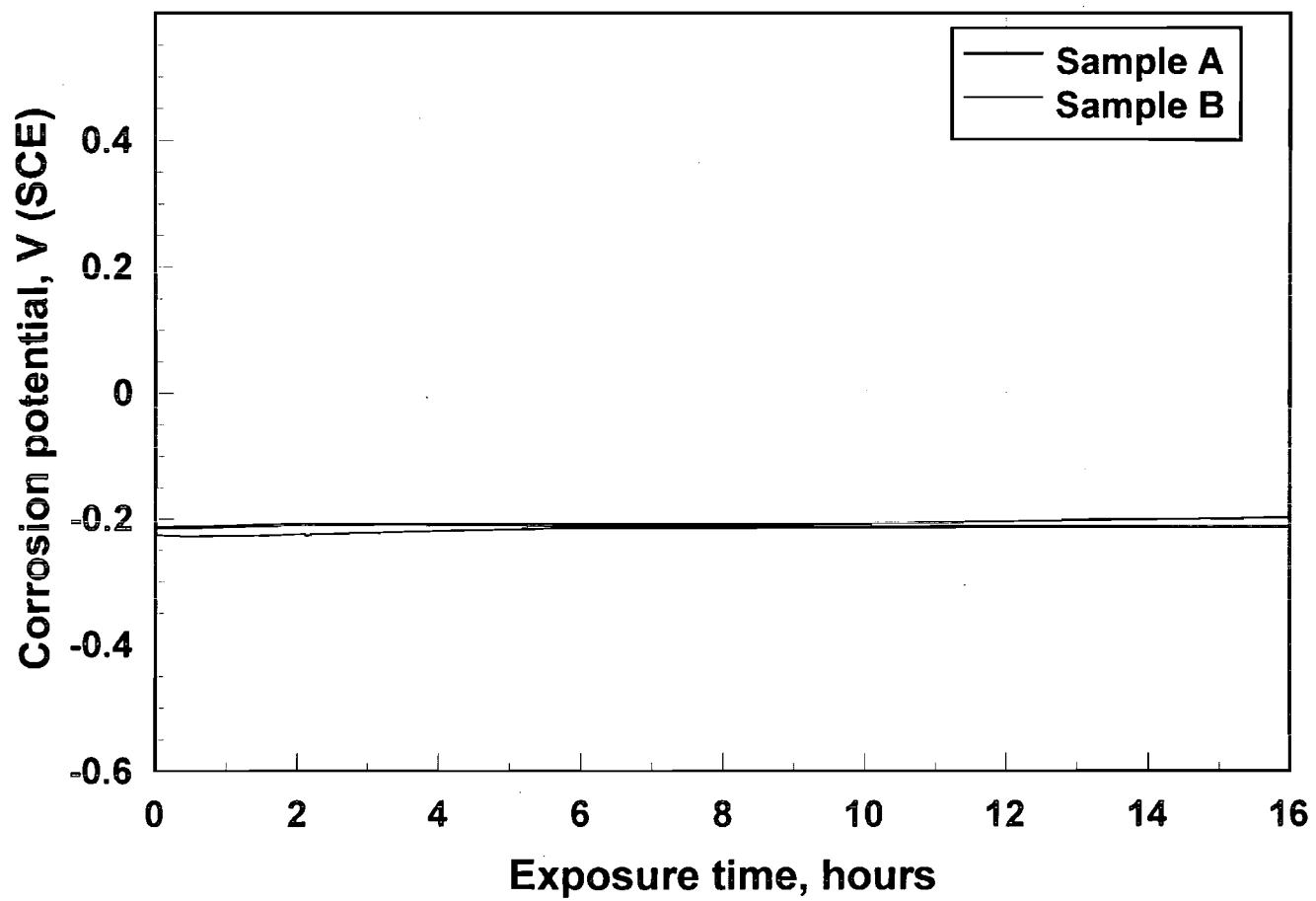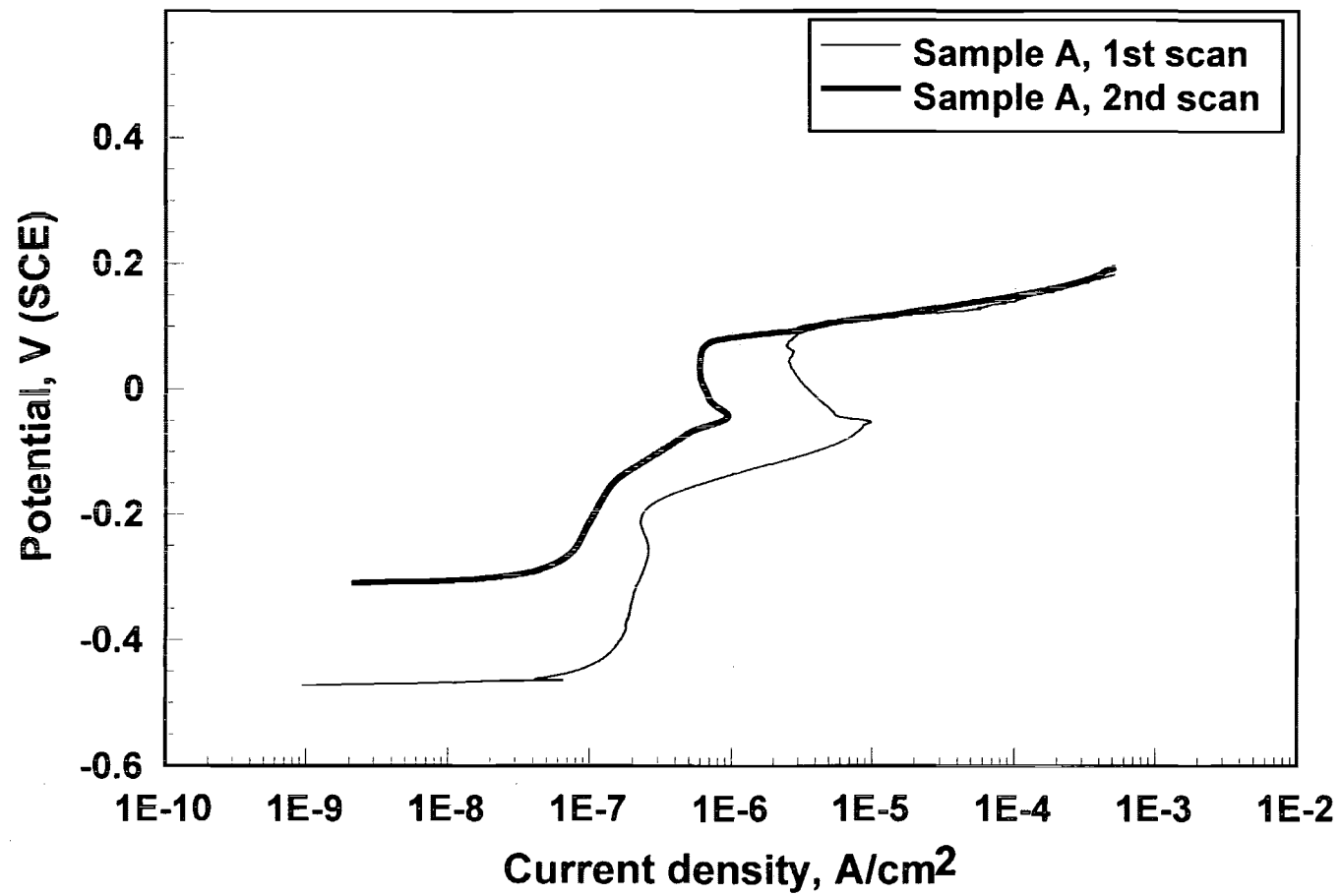
Study II - Fig. 1
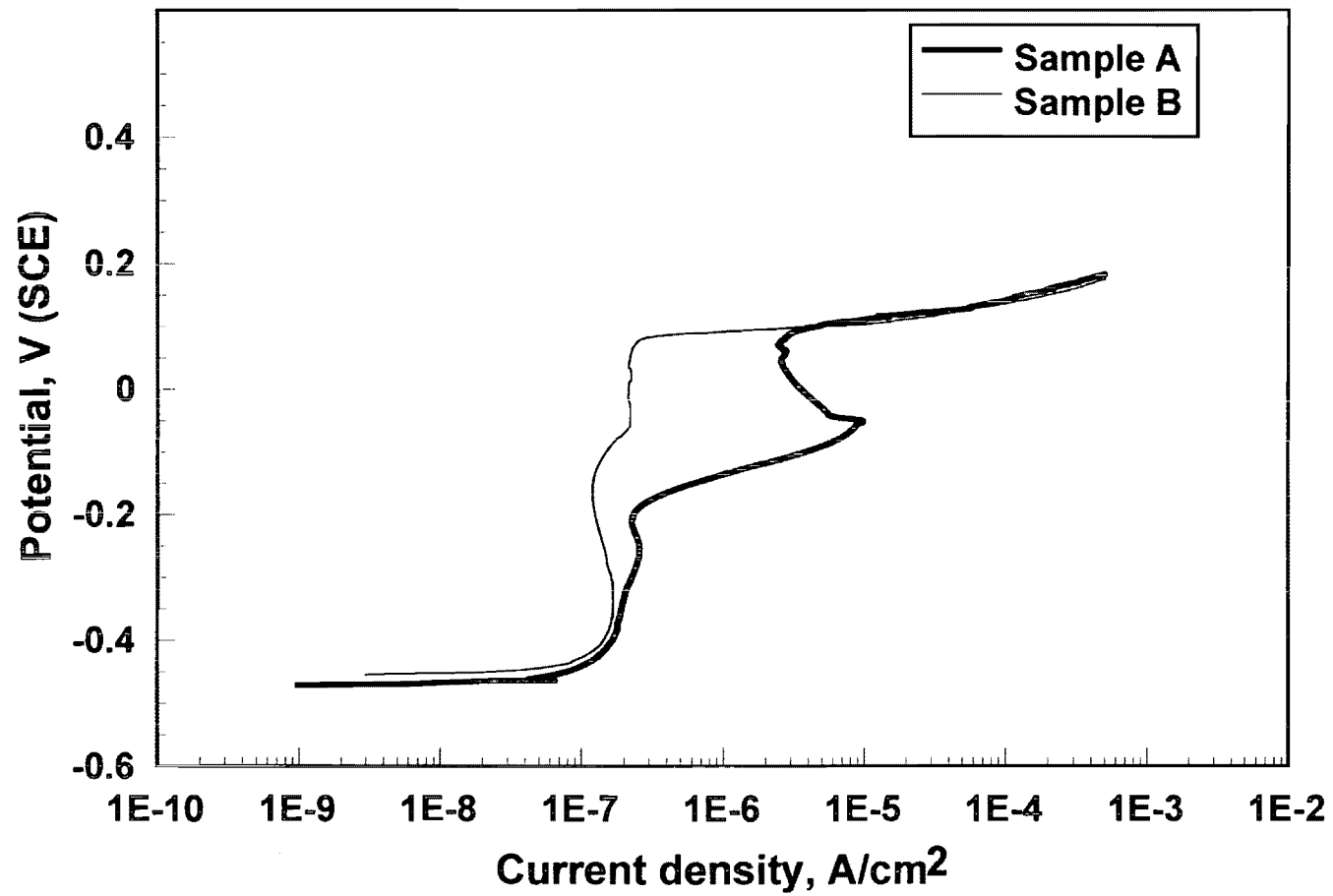
Study II - Fig. 2

Study II - Fig. 3

Study III

CORROSION POTENTIAL AND POLARIZATION BEHAVIOR OF CENTERLESS GROUND NITINOL TUBES

Specimens

Two tubes were received from C.R. Bard, Inc. They were identified as Sample C, ground using silicon carbide, and Sample E1, ground using cork wheel. Each tube was cut in two half-length specimens, which were prepared as electrodes (C#1 and C#2, E1#1 and E1#2).

Methodology

Both specimens were subjected to standard corrosion potential *vs.* time and potentiodynamic anodic polarization measurements. The procedures had been described in previously submitted protocols. The electrolyte was Ringer's solution, pH 7.4 at 37°C. For the corrosion potential measurements the electrolyte was saturated with a gas mixture containing 10% oxygen, 5% carbon dioxide, and balance nitrogen. For the potentiodynamic anodic polarization measurements the solution was deaerated using a gas mixture containing 5% carbon dioxide in oxygen-free nitrogen.

Results and Interpretation

The corrosion potential *vs.* time curves for all four electrodes are shown in Fig. 1. For both materials the corrosion potential showed a tendency to increase (become less negative) with time. The two SiC-ground specimens exhibited a very consistent behavior, the corrosion potential - time curves overlapping almost exactly. The cork wheel-ground specimens showed a more variable behavior and more negative corrosion potentials even after potential stabilization. One of the two cork wheel-ground electrodes showed a significantly more negative corrosion potential during the initial 2-hour exposure period, with fluctuations indicating corrosion activity, possibly due to contamination of the surface or a large number of small defects. At the end of the test exposure (16 h) the corrosion potentials were -0.117 and -0.114 V (SCE) for the SiC-ground specimens, and -0.131 and -0.143 V (SCE) for the cork wheel-ground specimens. The average corrosion potential maxima were thus less negative by about 10 mV for the SiC-ground specimens than the average corrosion potential maxima for

the biomedical devices tested earlier[2], and more negative by about 12 mV for the cork wheel-ground specimens than the biomedical devices.

The anodic polarization curves for all four tested electrodes are summarized in Fig. 2. All specimens exhibited very similar behavior, the SiC-ground specimens showing again more consibiomedical device results. All specimens showed a relatively wide range of passivity followed by a breakdown. For the SiC-ground specimens the breakdown potentials were 0.489 and 0.438 V (SCE) for Specimens C#1 and C#2, respectively. For the cork wheel-ground specimens the breakdown potentials were 0.400 and 0.492 V (SCE) for Specimens E1#1 and E1#2, respectively. Specimen E1#2, however, showed some activity below the complete breakdown, starting at about 0.380 V (SCE).

The breakdown potential data can be compared with the mean breakdown potential of 0.030 V (SCE) (S.D. 0.040, range -0.045 to 0.096 V, SCE) for the biomedical devices tested previously [1]. This comparison shows an increase in the breakdown potential value by about 0.43 V for the SiC ground material based on the average values, and 0.34 V for the lower of the two values above the highest breakdown potential measured for the biomedical devices. This increase in the breakdown potential indicates a substantially improved resistance to initiation of pitting. For the cork wheel-ground specimens there was a similar improvement, but all the results were less consistent and generally inferior to those for the SiC-ground tube.

The breakdown potentials measured in this study were above the redox potential of the solution, and close to the theoretical thermodynamic maximum. It is thus highly unlikely that pitting would initiate in a similar environment on identically prepared surfaces, as long as they are free from shieldng that would create crevice corrosion conditions.

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[2] M. Marek: Corrosion behavior of Biomedical Products in Ringer's Solution. First Addendum. Test Report submitted to C.R. Bard, Inc., June 18, 1996.
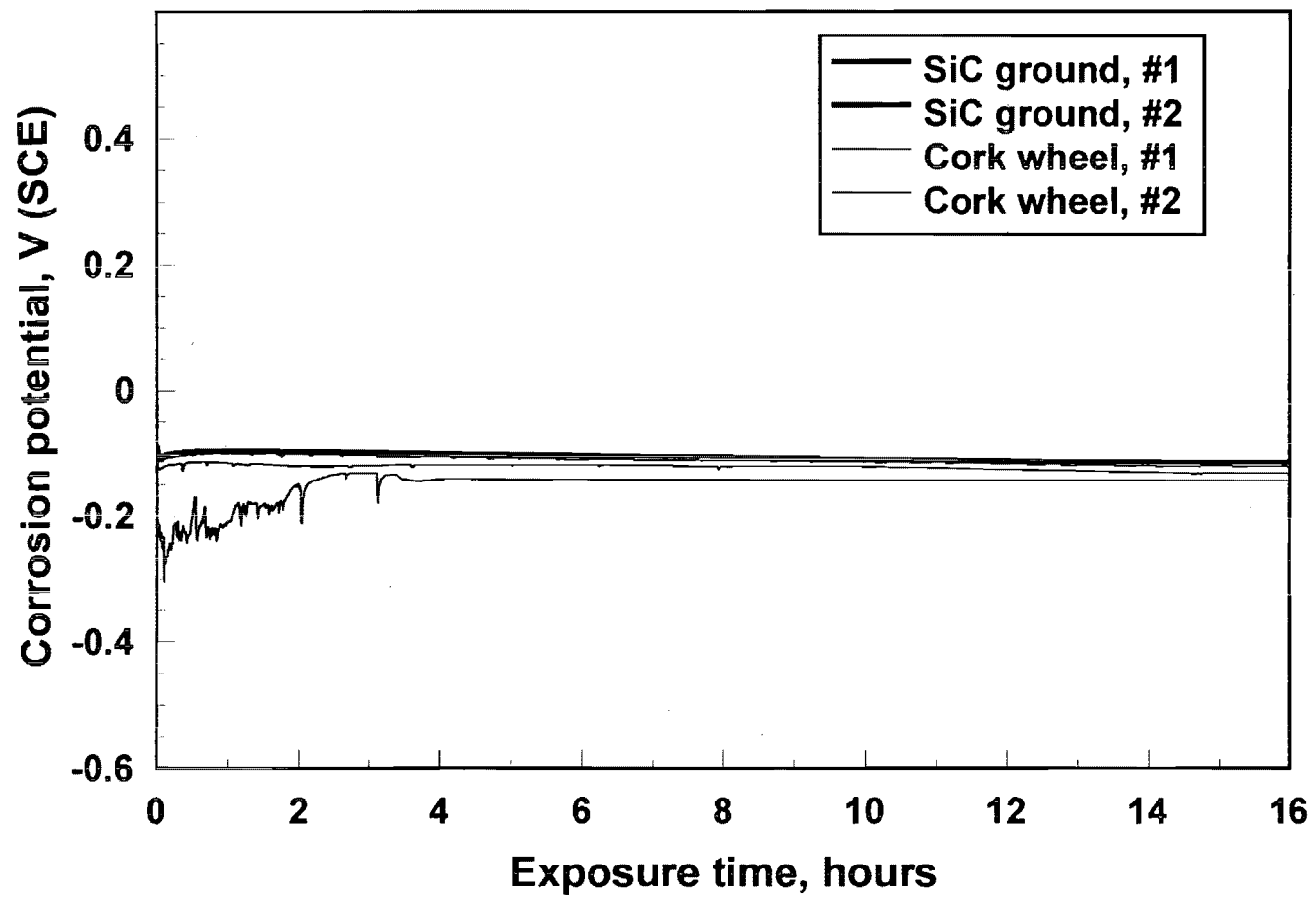
Study III - Fig. 1
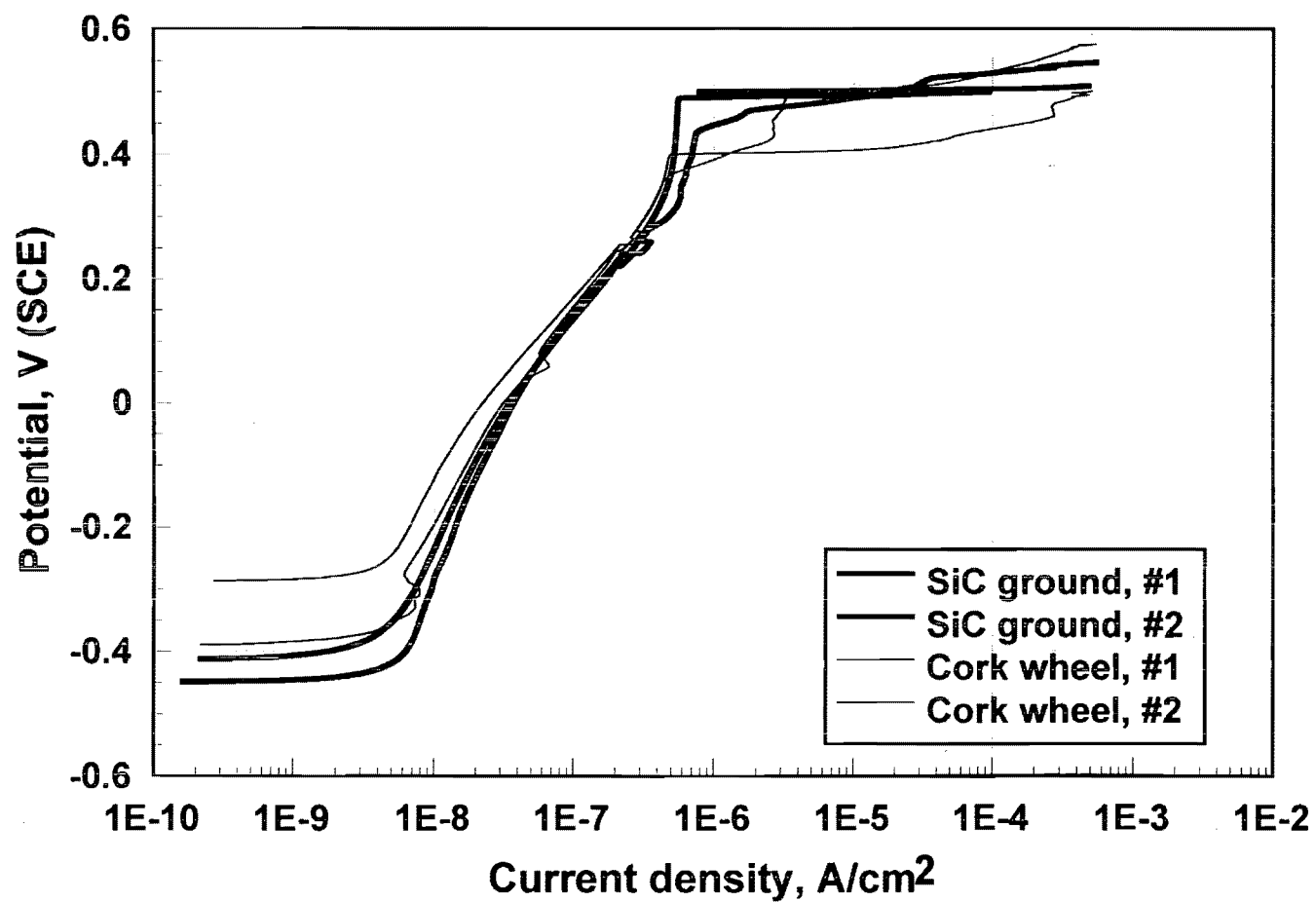
Study III - Fig. 2

Study IV

CORROSION EVALUATION OF BILIARY BIOMEDICAL DEVICES IN PORCINE BILE EXTRACT SOLUTION

Table of Contents

1. OBJECTIVES

The objective of the test program was to evaluate the short-term corrosion behavior of three types of biliary biomedical devices under conditions simulating the environment of the implants in the human body, using electrochemical test methods.

2. TESTED DEVICES

The following biliary biomedical devices were received from Bard Radiology Division for testing: Type A (6 each), Type B (6 each), Type C-1 (3 each) Type C-2 (3 each).

3. METHODOLOGY

The short-term electrochemical tests of the corrosion behavior included corrosion potential *vs.* time measurements, and potentiodynamic anodic polarization scans. The tests were performed using a 9% porcine bile extract solution as a bile substitute, at 37°C. The atmosphere, maintained above the solution, was a gas mixture containing 6 % oxygen, 5% carbon dioxide, and balance nitrogen. All potentials were measured with respect to a standard Saturated Calomel Electrode (SCE). The tests followed the previously submitted and approved protocols.

4. TEST RESULTS

4.1 Potential *vs.* Time

The total exposure time was 15 h. The replicate data for each type of biomedical device have been compiled and plotted in Figs. 1-3. The replicate data also have been averaged by calculating the mean of the corrosion potentials at each data point, and the results for the three types of biomedical devices have been plotted in Fig. 4.

All test have shown a relatively stable potential during the first hour of exposure. For Type A biomedical devices the average potential in this time period was -0.177 V (SCE), and ranged from -0.223 to -0.136 V (SCE). For Type C device devices the average

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potential in the initial 1 h period was -0.104 V (SCE) and ranged from -0.154 to -0.056 V (SCE). For Type B biomedical devices the average potential in the initial 1 h period was +0.043 V (SCE), and ranged from -0.020 to +0.072 V (SCE).

After the initial period of relatively stable values the corrosion potential showed a transition to lower (more negative) values. The transition was especially sharp for Type A and Type C devices, where the total change was more then -200 mV. The Type B devices showed a milder and more gradual potential drop of about -90 mV over the total 15 h exposure period. When the solution was exchanged for a fresh one at the end of the 15 h exposure period the corrosion potential recovered to approximately the initial value. This indicates that the potential drop was due to degradation of the solution rather than surface changes of the materials.

4.2 Potentiodynamic Anodic Polarization Curves

The replicate data for each type of biomedical device have been compiled and plotted in Figs 5-7. The replicate data also have been averaged and the results for the three types of biomedical devices have been plotted in Fig. 8. For the plots in Figs. 5-8 the cathodic portions of the polarization curves have been deleted, and numerical smoothing was used to remove transient peaks, which were artifacts caused by autoranging. Averaging was performed by calculating the mean current density at each potential, and the average curves were plotted only for the potential range where all six replicate tests generated data points.

All three types of biomedical devices exhibited passivation behavior (Figs. 5-8). Type A and Type C devices showed very similar polarization curves, except that the current densities were about an order of magnitude higher for the Type A biomedical devices than for Type C devices. Type B devices showed a pronounced and reproducible current peak at about +0.72 V (SCE). None of the devices showed a breakdown of passivity within the physiological range of potentials. At high potentials (above 1 V, SCE) the current density increased with increasing potential, probably due to electrolysis of water and evolution of oxygen.

5. STATISTICAL PROCEDURES

Since none of the tested biomedical devices exhibited breakdown of passivity, the statistical treatment described in the protocols was not applicable. The only statistical treatment performed was the averaging described above.

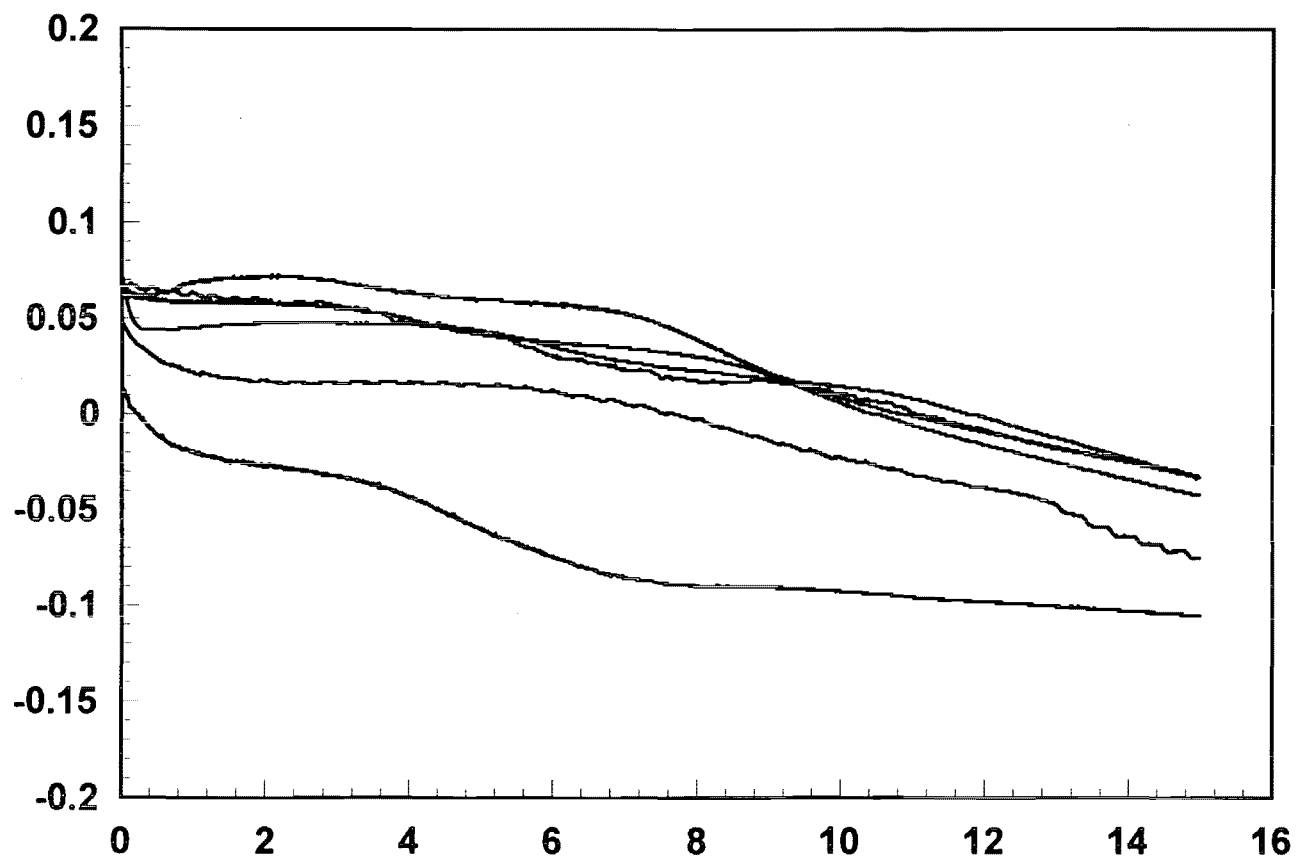## 6. EVALUATION OF THE RESULTS

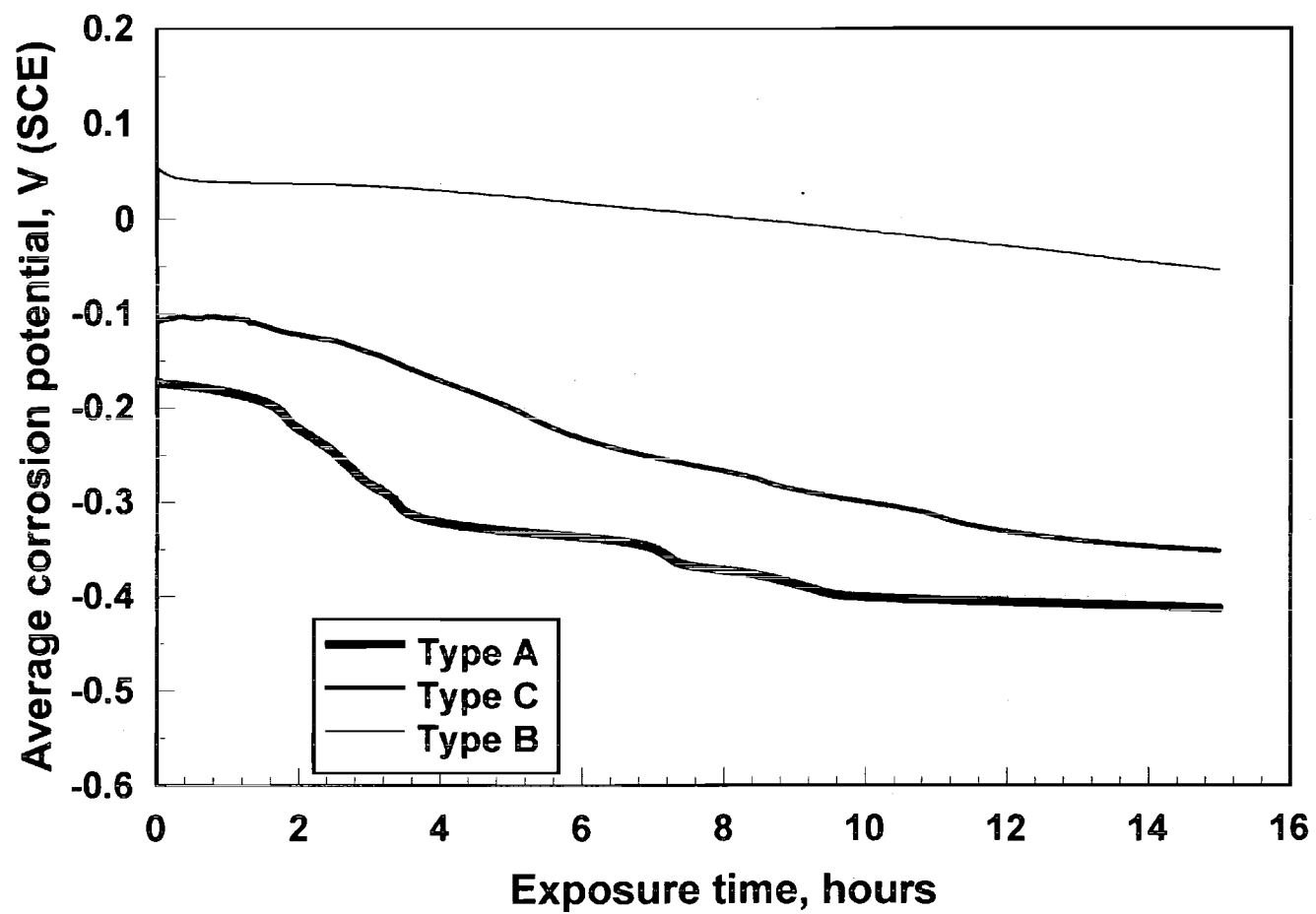As specified in the Protocols the test results will be analyzed by the study sponsor.
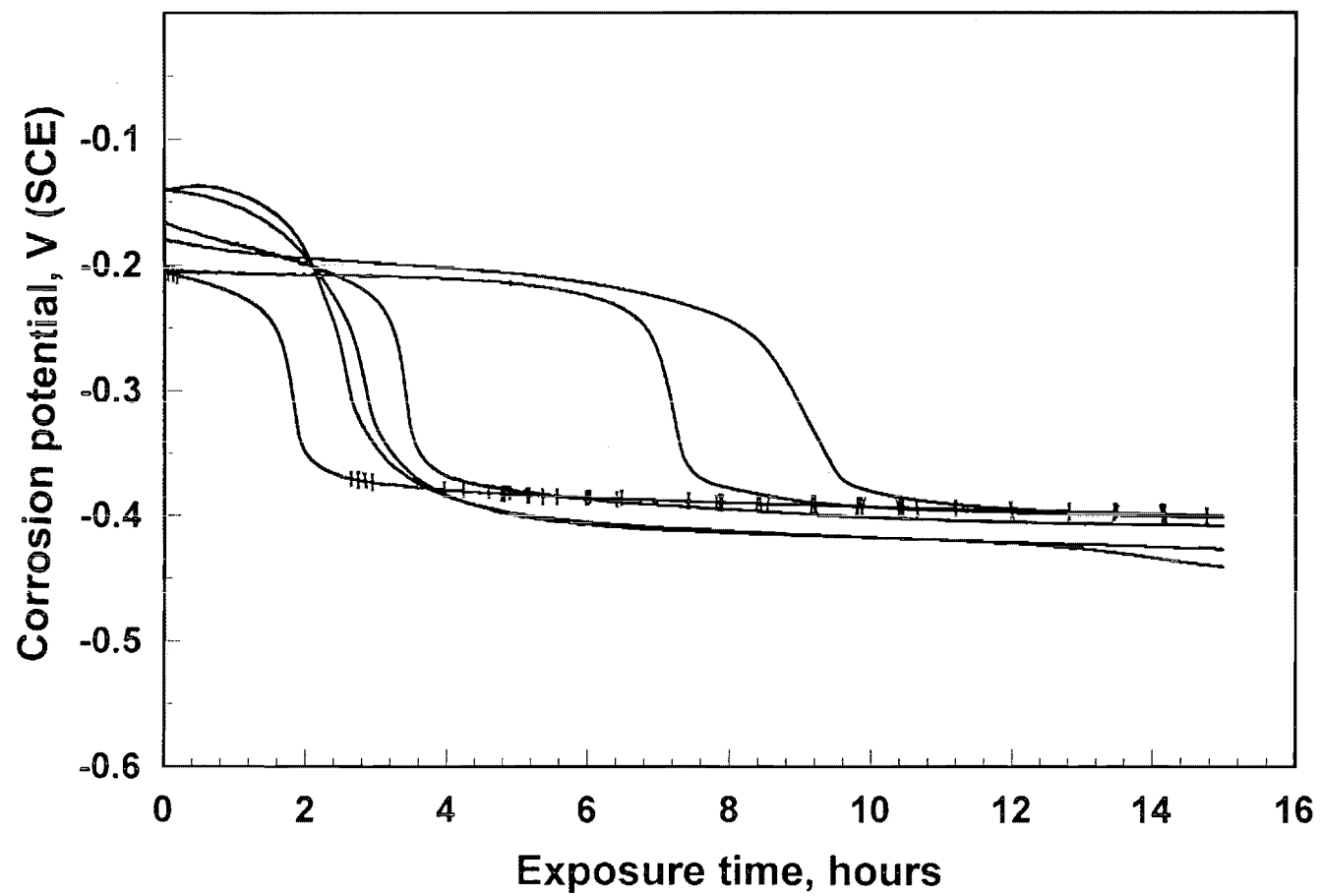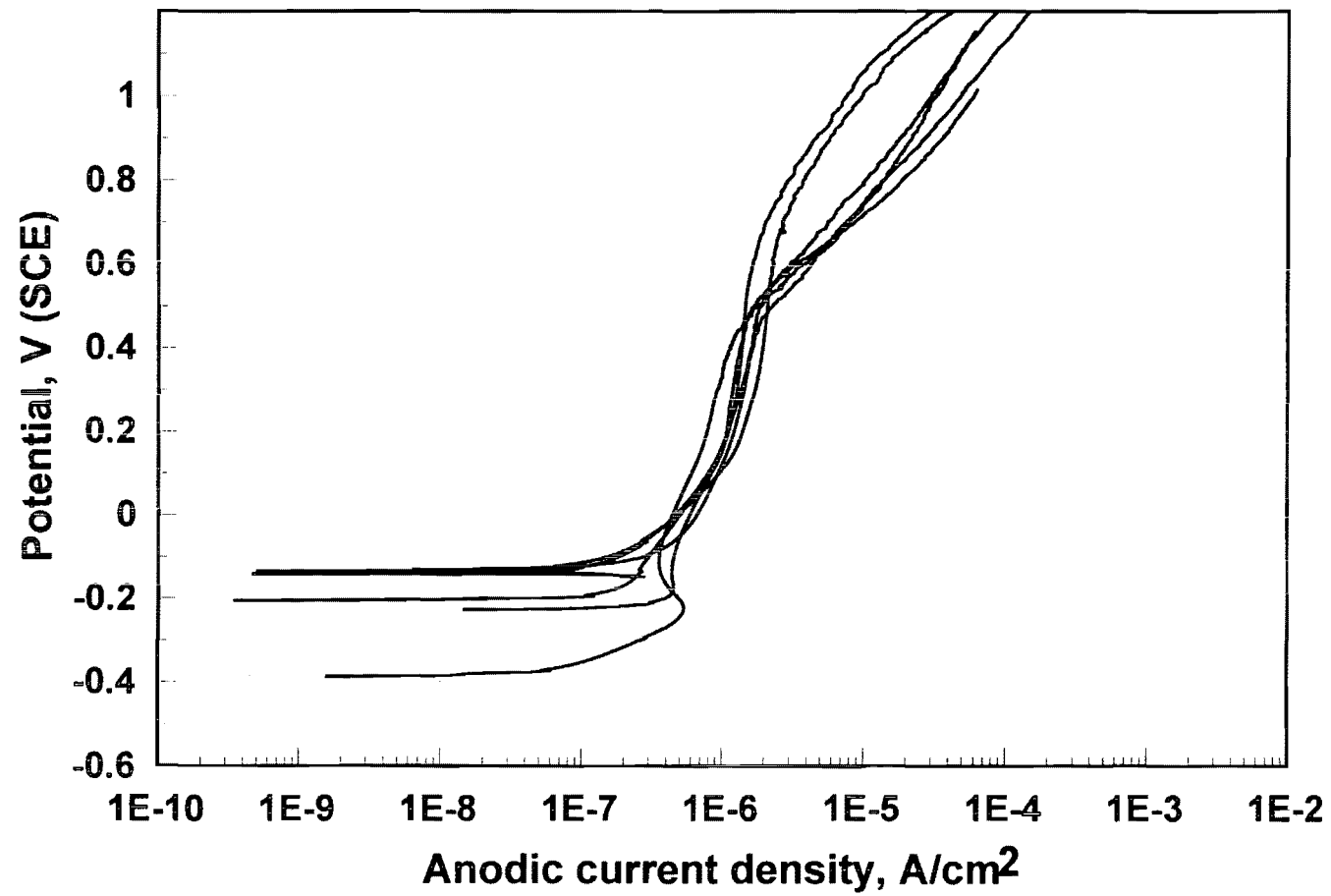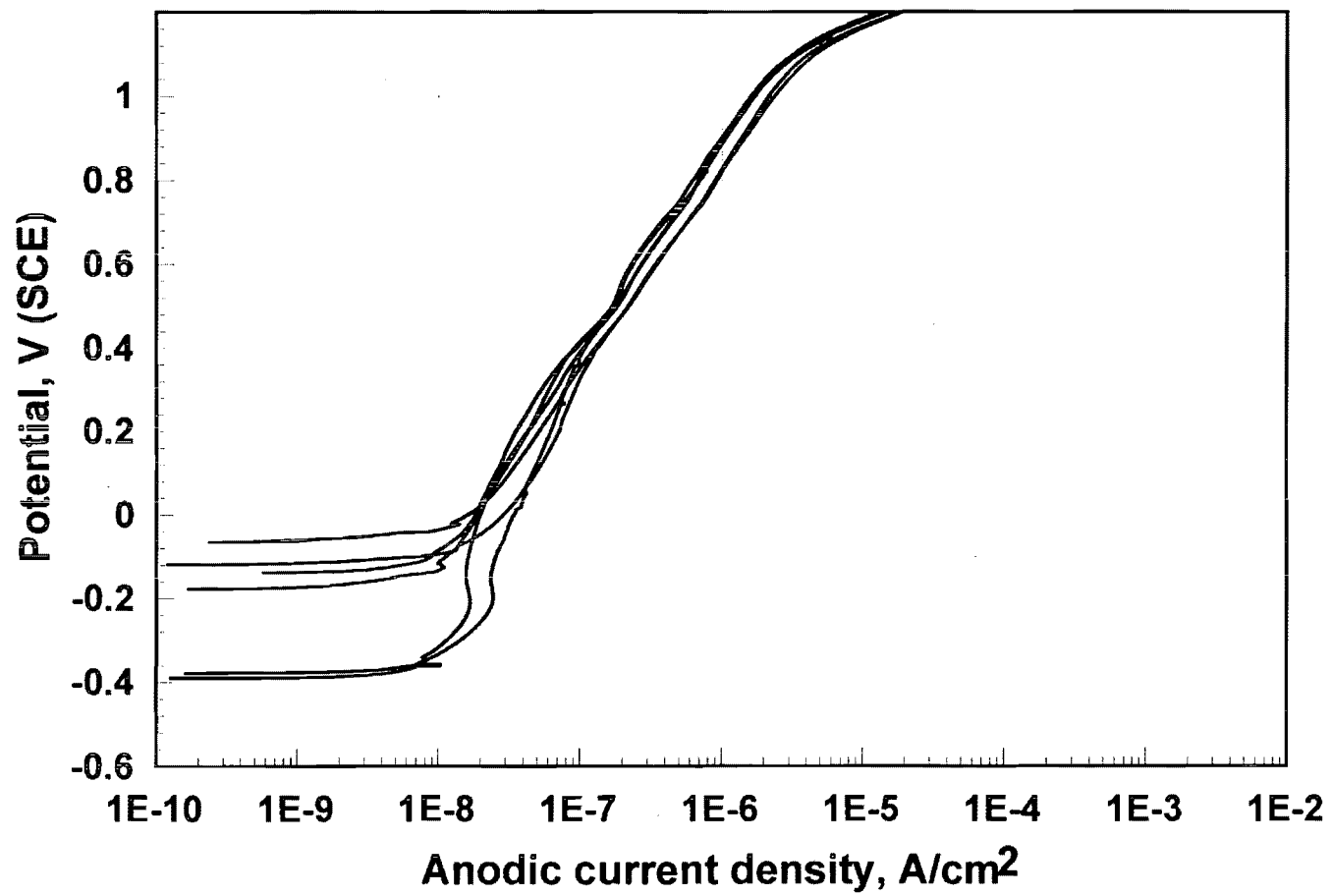
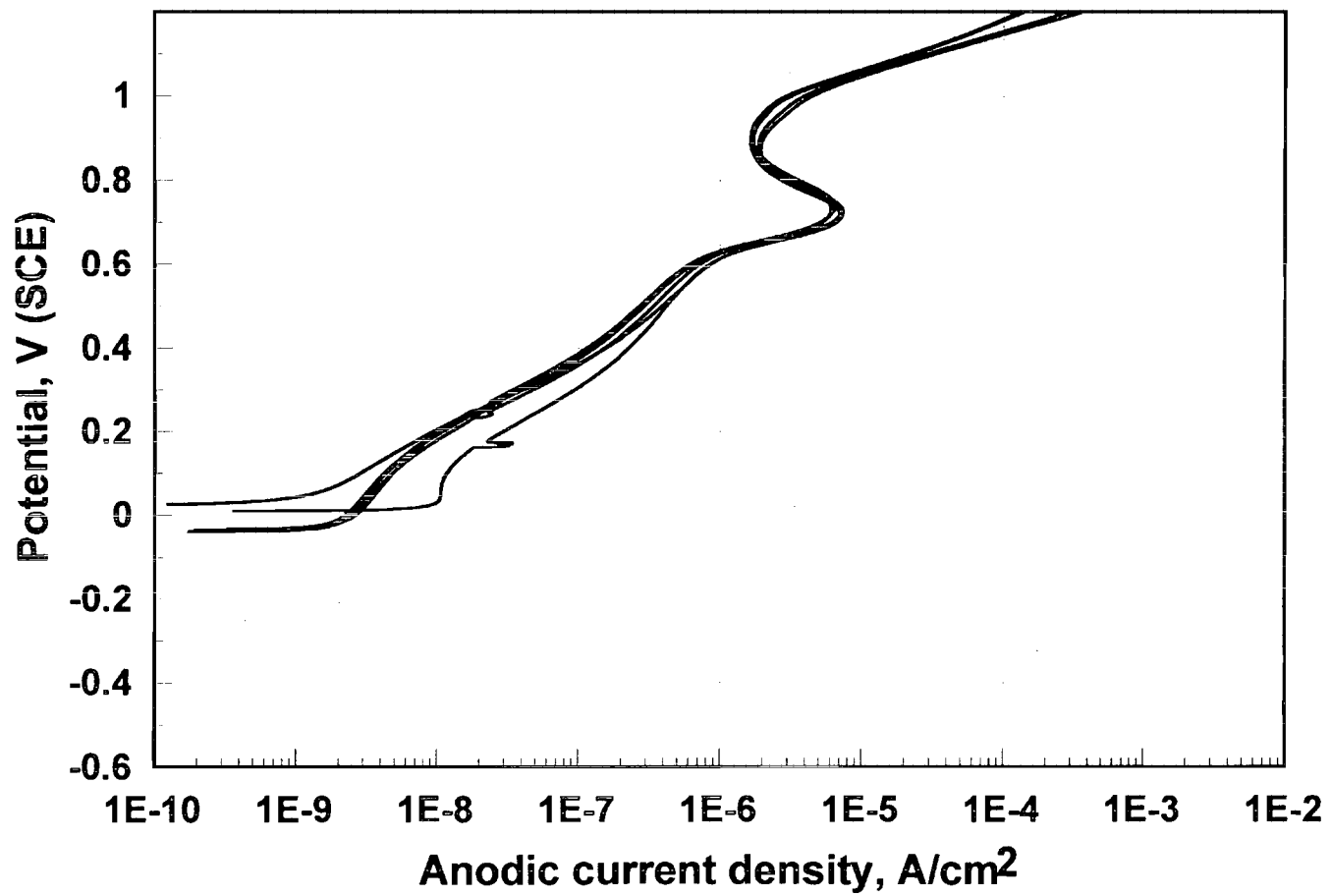Study IV - Fig. 1
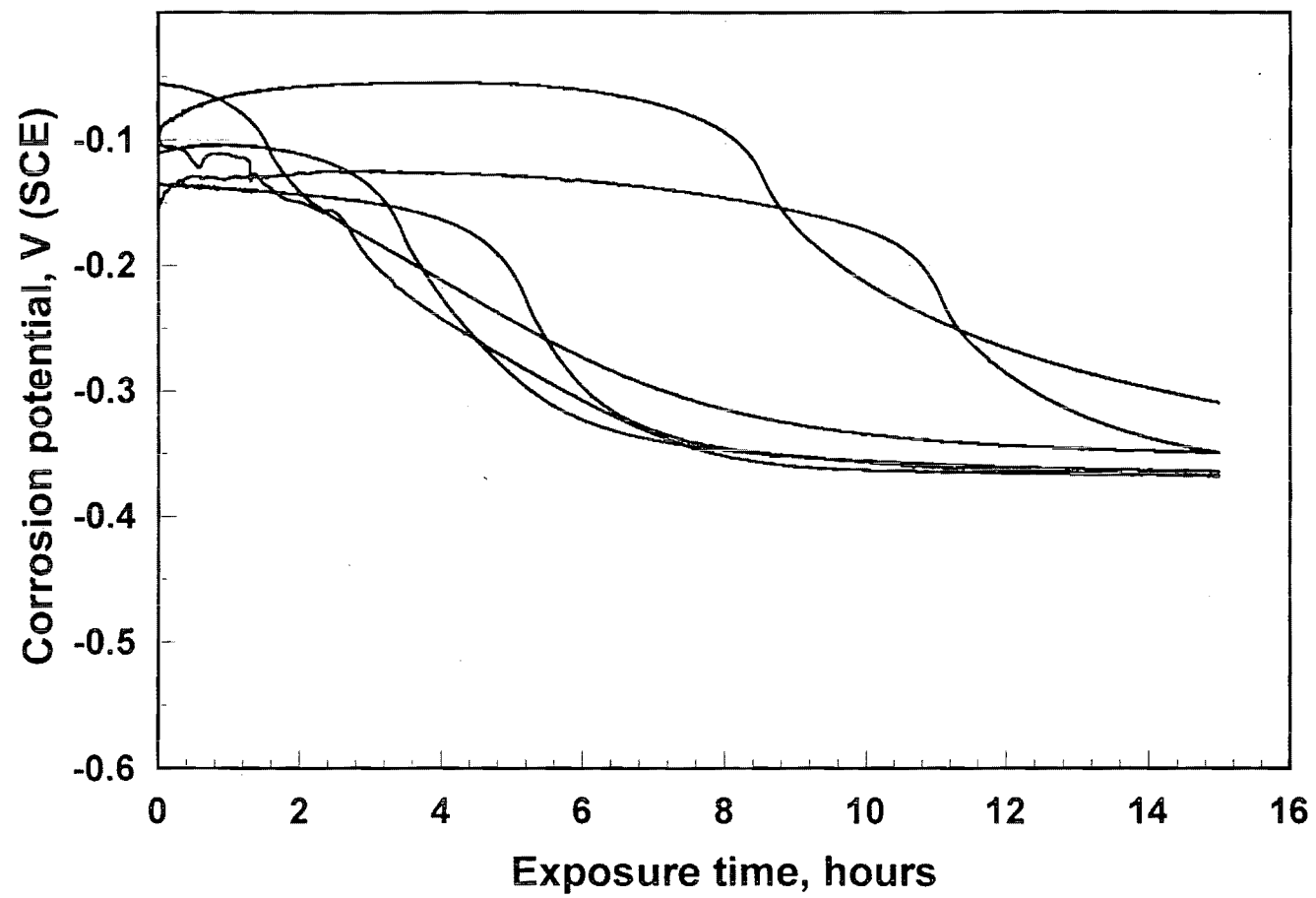
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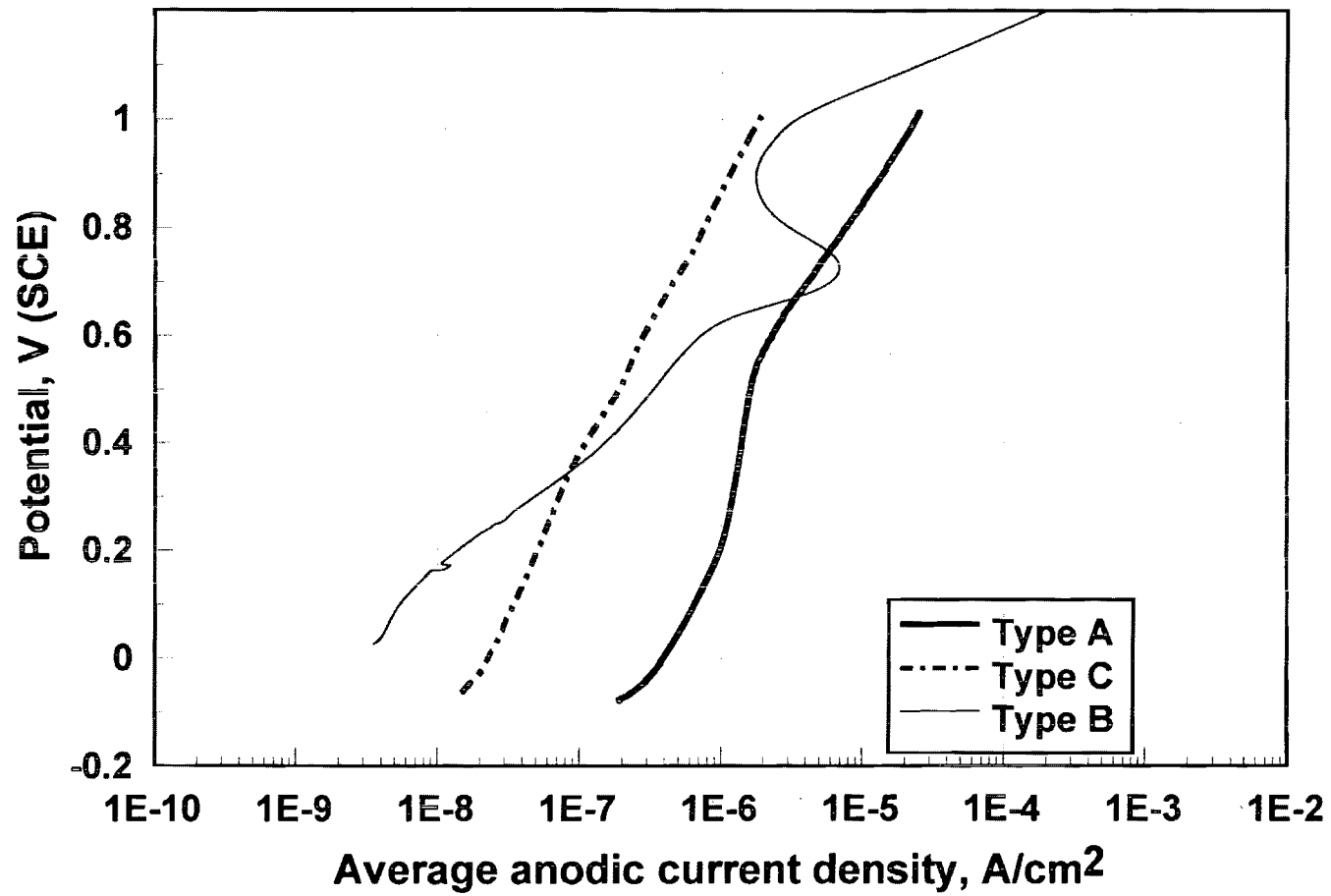
Study IV - Fig. 3

Study IV - Fig. 4

Study IV - Fig. 5

Study IV - Fig. 6

Study IV - Fig. 7

Study IV - Fig. 8