THE UNIVERSITY OF MANITOBA

EVALUATION OF A PRECIPITATION HARDENED WROUGHT

COBALT-NICKEL-CHROMIUM-TITANIUM ALLOY FOR SURGICAL IMPLANTS

By

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A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

OF MASTER OF SCIENCE

DEPARTMENT OF MECHANICAL ENGINEERING

WINNIPEG, MANITOBA

MAY 1978

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A dissertation submitted to the Faculty of Graduate Studies of
the University of Manitoba in partial fulfillment of the requirements
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ACKNOWLEDGMENTS

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Orthopedic surgery is a science which is in a perpetual state of development. The instruments necessary to assist the surgeon in his task are always subject to study and improvement. One of the main instruments is the surgical implant.

The challenge encountered in the search for the ideal surgical implant is caused by the conditions under which it must perform. An ideal implant should meet the following requirements:

1. have sufficient static and fatigue strength and wear resistance for the application

2. be non toxic, non allergenic and non carcinogenic

3. be non corrosive in the physiological environment

4. have no effect on the host tissue, bone or body fluids.

A chapter of this thesis is reserved for the study in chronological order from the 1930's to the present, of the research and experimentations which have led to today's prosthesis and outlines the problems which still remain to be solved because of what is asked of a surgical implant.

The stringent requirements for implant alloys severely restricts the types of alloys which might be used. For the most part, pure metals or single phase alloys have been selected because these materials generally exhibit superior corrosion resistance. However, restricting implant alloys

2.

to pure or single phase materials limits the strength of the material in that the only strengthening mechanisms which can be utilized are solid solution strengthening, cold working, and grain size control. The use of precipitation hardening alloys for surgical implants offers the potential for obtaining higher strength materials but their use has been avoided probably because of a fear of poor corrosion resistance and resultant deleterious effects on the body environment.

The development of a precipitation hardening superalloy [8] containing 40% Co, 37% Ni, 18% Cr, 5% Ti, all elements which have proved acceptable for surgical implants, suggests that this alloy may be suitable for implant applications. A study of this alloy was therefore conducted to evaluate its potential for use as an implant alloy. The parameters investigated were:

1. Static strength
2. Fatigue strength
3. In-vitro corrosion resistance
4. In-vivo corrosion resistance.

CHAPTER 2

REVIEW OF THE LITERATURE

2.1 Implants and Their Problems

Abstract

Orthopedic surgery has been performed for hundreds of years, and was of great interest in the 19th century. But it was not until the years 1940 - 1950, the "war and post war years", that concern and improvement appeared in the design and choice of materials for implant purposes. The following is a survey, in chronological order, of the successes, failures, and problems created by implants and subsequent improvements that led to today's orthopedic devices and surgical techniques.

2.2 Literature Review

Implants were first used to repair broken bones, and in 1930 the first internal prostheses, made of mild steel, were tested with fairly good results, but corrosion was often reported.

In the year 1950, the use of implants was more widespread, and metallic devices were sometimes used for different purposes, one of those purposes being femoral lengthening [20]. The latest gave very few encouraging results, and when failure occurred, no mention was made of the possibility of an implant failure.

In 1951, the implants, then called internal fixation or internal prosthesis, seemed to give fairly encouraging results, even if the breaking

of some of those devices [21] was often reported. Still very little was said about the standard requirements of those devices.

In 1952, rapid improvements were made in hip joint surgery, especially when a new device appeared as a surgical implant. This new implant, the "door knob prosthesis" [22] was screwed into the medullary canal and was reported to be made of either vitallium or stainless steel, type 317. Its inventor, Dr. McBride, described it as a hip joint prosthesis composed of a spherical head, a neck, and a threaded intramedullary stem.

For this implant material, Dr. McBride chose either stainless steel type 317, or vitallium. The reason for his choice was that the above were "dependably non-electrolytic", in other words, corrosion resistant.

As the use of metallic implants was growing, so grew the concern for the "non-electrolytic" quality of the materials used. Of all the studies, one of the most remarkable, for its concern of the metallurgical problems involved, was that of Dr. P. G. Laing on the corrosion resistance of the orthopedic implant [23]. In this article, it was said that: "Certain metals and alloys with suitable strength for orthopedic purposes are more resistant to corrosion than others under the special conditions existing in the human body. Of these, stainless steel, known as AISI #316, and the cobalt, chromium, molybdenum alloy known as vitallium are in common use." In the same article, factors encouraging corrosion in the body were equally listed, mainly mixed metals, fretting corrosion,

differential aeration. Experiments were made on rabbits, and the corrosion of orthopedic screws was measured by weighing before and after insertion in the animal, and by doing histological studies of tissues around the implants. It was concluded that the metallic transfer from screwdriver to screw appeared to adversely influence the corrosion resistance of the screw and the composition of the driver would have to be related to that of the screw.

During the same period, in England, Dr. J. Cohen was working on foreign body reactions. His method consisted in metal powder injection inside living organisms. The result of his work showed that only a few metals and plastics were inert, the inertness being relative, because in the form of fine powders, even those materials considered least provocative of inflammation would cause appreciable tissue reaction. The conclusion of his work showed that the least corrosion was reported when a powder alloy made of chromium and cobalt was used. It also showed that mild steel gave very violent tissue reactions.

Dr. J. Cohen pointed out the danger of corrosion products in a human organism, when he reported in another article [24] a case of fracture by corrosion of a Smith Peterson nail - Thornton plate, made of stainless steel, which caused the death due to necrosis of an elderly lady; infection, and a massive heart failure, a pattern unfortunately too well known today with elderly patients suffering from implant failures.

Meanwhile, Dr. Laing completed a study [25] in applied metallurgy on the contamination of implants. His conclusions were that the 2 factors

involved in the process of contamination were:

1) Metallic transfer.

2) Flaking of large pieces of the tip of the screwdriver by the cutting action of the screw slot against the screwdriver.

At the beginning of the 1960's, Dr. Ferguson and Dr. Laing reported experimental evidence that ionization occurs around all types of metallic alloys currently in use in human bodies, regardless of how resistant to corrosion these alloys are thought to be [26].

Meanwhile, Dr. Cohen reported on another case of failure by corrosion [27], this time from a Steinmann pin used for intramedullary fixation. It was established that the cause was the choice of dissimilar steels for screws and pins, the screws being made of AISI type 316 stainless steel and the pin of a type 420. It was determined that the composition of the steel was the principal fact in promoting corrosion, although cyclic stresses and non-metallic inclusions probably influenced the localization of the corrosion process.

By 1960 - 1962, already 30 years had passed since the first orthopedic devices had been implanted, so the first long range studies of implant behavior were now possible. In one of the studies [28] the tendency of implants to provoke wound reactions was analyzed. In this particular study, the cobalt-chromium alloy proved to be the better, the incidence of obligatory removal being at most 3%, while the 18/8 molybdenum stainless steel proved to be the poorest, with an incidence of 20%.

In March 1962, Dr. J. Cohen tested the corrosion resistance of vitallium and AISI type 316 stainless steel under condition of cyclic stress, in vitro. Vitallium showed the greatest corrosion resistance under those experimental conditions [29].

Meanwhile, Dr. Laing and Dr. Ferguson started a study of the trace metal ion concentration in the liver, kidney, spleen, and lung of the normal rabbit. This study of normal trace ion concentration for 4 major organs in the rabbit was done to provide a baseline against which a rise in concentration of ions could be determined when the experiments were varied. During the same month, they published another study of ion concentation for 4 major organs, but this time with imbedded metal implants in rabbits [30]. The results of this study showed that stainless steel contributed nickel to the body circulation, and cobalt based elements contributed cobalt. The spleen was found to be the most active site of trace iron storage - the other organs, especially the liver, tending to get rid of an early increase in concentration. Cobalt and nickel were the most active ions in terms of their presence in these organs.

In 1964, a study and survey of 455 patients was made on the use and justification of acrylic cement in the bonding of prosthesis [31]. It was reported that no sign of deterioration of the bond between the cement and bone had been seen in histological preparation up to three and a quarter years after the operation, and no harmful effect had been recognized or suspected in the patients in whom it had been used. The technique was considered justifiable in elderly patients when the medullary canal is large and the cortex of the femur is thin and brittle.

Of course, as problems in orthopedic surgery increased, some standards for implant materials had to be defined [32] and the validity of the whole process had to be discussed [33]. The F4 (Surgical Material) Committee of the ASTM held a meeting in Cleveland (Ohio) on April 20, 1967, to develop specifications for materials to be used in surgical implants and to develop procedures with regard to testing and handling the like. In the same meeting, in reply to Dr. A. Dawkins who had seen in Russia massive replacement by cadaveric bones, it was said that metal replacement promised a better and quicker result.

In the middle 1960's not every problem encountered in orthopedic surgery was solved [34]. For example, the management of advanced degenerative arthritis of the hip, especially when bilateral, remained unsolved. But the vitallium cup arthroplasty pioneered by Smith-Peterson in 1939 had been refined and its indications, scope and results well documented [35].

Medullary stem prosthesis of vitallium had proved satisfactory and of these the Austin-Moore and Thompson design were the ones most commonly used for degenerative arthritis. This method showed a variable degree of improvement in all patients. There was a worthwhile improvement in functions and relief of pain, but stability was disappointing in more than half the cases (and in all the bilateral cases) and an average of 3/4 of an inch of shortening was found in the unilateral cases. The conclusion was that the use of the Austin-Moore prosthesis with acetabular reaming had very limited indications.

In the same month, an article appeared on the replacement of arthritic hips by the McKee-Farrar prosthesis. It was noted that "it

seemed obvious that the chromium-cobalt alloy had decided advantages over stainless steel." The joint consisted of two components; the femoral, which was a standard Thompson prosthesis, and the acetabular reaming which was a hemispherical cup lapped in to fit the head of the Thompson prosthesis. The results were encouraging, showing a success rate of 90%.

In 1966, there appeared an article that showed concern about the effect of metal implants inside the human body [36]. The author stated that "the liberation into tissues of the product of corrosion of various pure metals and of alloys used for surgical implants has been shown by spectrochemical analysis [37], and the presence of those products has been thought to explain:

1) the persistence of infections in the presence of surgical implants

2) the occurrence of an apparently sterile inflammatory response to metallic implants

3) persistent pain in relation to an implant."

In summary, this study shows that the corrosion of an 18% Cr, 8% Ni, 3% Mo stainless steel implant, and of some pure metals, may affect not only the surrounding tissues but also the individual cell. Also metallic contamination from surgical tools was confirmed.

Later, the toxicity of metal particles of several corrosion resistant alloys, mainly stainless steel and cobalt chromium alloy [38] was investigated by exposing tissue cultures to powders of these alloys

and counting the cell population after standard replication intervals. The difference in the degree of toxicity of these alloys, not demonstrated by "in vivo" method was elicited. But in Part II of the same paper [39] the same procedure was repeated with a significant difference, the counting of cells now being made in the lag phase rather than in the replica phase. Several metals used in orthopedic surgery and known to be well tolerated in tissues, clinically were shown to have significant toxicity for tissue culture cells, the cobalt-chromium alloy being more toxic than the stainless steel of type 316. Tissue culture cells containing materials derived from the alloy (corrosion products) were observed in mitosis and cells so labelled survived as many as 15 sequences of subculture.

These results seemed to be confirmed when in 1968, during a study on a vitallium-hinge artheoplasty performed according to the method described by Young, the inertness of vitallium is questioned [40]. Clinically the patient had no complication or chemical evidence of tissue reaction, but pathologically a massive amount of prussian blue positive staining material was found in the capsule and lining the canal formed by the stem of the prosthesis. Mechanical wear or corrosion was evident at the area of contact and on the central axis of the hinge. But still difficult operations are performed with the help of metallic implants, like in the case of a massive osteolysis (vanishing bone disease) of the humerus treated by resection and prosthetic replacement by Dr. H. Poirier. In this particular case the diseased bone was resected leaving only the lower part of the humerus, and replaced with success by a titanium prosthesis.

At the same time, Dr. Homsy presented a study on corrosion of SMO stainless steel fracture fixation plate showing them to be susceptible to crevice corrosion. It was shown that the introduction of a polymeric stress membrane helped to lessen the incidence of interaction between the screw and the plate without altering the stability of the fixation device. Two years later, in another study, Dr. Charles and Dr. Homsy noticed that there was a tendency of apposed tissues and bones to become tightly adhered to the implant and that these adhesions complicated removal of symptomatic appliances [41]. On this basis, surface roughness and surface energy were reduced by filling surface pores with teflon TFE which seemed to reduce the tendency for intimate adhesion of the cellular environment of the implant. During the same year (1968) J. R. Cahoon and H. W. Paxton published in the Journal of Biomedical Materials Research a study on metallurgical analyses of failed orthopedic implants [2] which showed that fatigue was one of the major sources of failure and that fatigue was a result of poor design or poor material, and stressed the importance of an efficient control of fabrication at the manufacturing level to insure that the A.S.T.M. specifications control metal content and porosity of implants.

In February 1970, on a study made in Vietnam, the use of metallic internal fixation in the primary treatment of 176 open skeletal injuries was discussed and the results demonstrated that the use of stainless steel in this type of injury had no harmful effect. It can be used with safety and benefit in the primary treatment of open skeletal wounds especially in the multiple and complicated injuries of war and motor vehicle accidents.

The same year, J. R. Cahoon and H. W. Paxton published a metallurgical survey of current orthopedic implants [17] showing over 50% of the sampled current orthopedic implants contained metallurgical or design deficiencies similar to the ones which have been known to cause failure. It was suggested that rigorous inspection procedures at the manufacturing level be established to insure that defective implants are not marketed. In 1971, a fiber titanium composite was developed [42] and its potential application as a method of skeletal fixation for internal prosthetic devices had been studied and found quite satisfactory, as it would provide fixation to bone and uniform stress distribution at the implant bone interface.

By June 1971, an orthopedic technique, the closed intermedullary nailing of the femur method, promoted by Dr. K. Clawson, was considered safe for treating most femoral-shaft fractures and for obtaining early functional recovery, no infections or non-unions were reported. During the same period, the technique of artheography, that is, the technique of total hip replacement was widely accepted. The devices used for this purpose were either of the type McKee-Farrar with vitallium to vitallium bearing, or of the Charmley's one (high density polyethylene to stainless steel bearing). Patients with persistent pains after total hip replacement of the hip were reported, but the cause was not clearly defined as very few loosenings of the prosthesis were reported.

In February 1972, the metal failure of a Küntsher nail, reported by Dr. Critchley, created new problems. The nail was made of 18/8 SMO steel and the analysis showed it to be low in molybdenum and to have more

non-metallic inclusions than control implants. The importance of pro-
tecting the highly polished surface of all metal implants during auto-
claving, handling and insertion was stressed.

In February 1973, an article was published on Smith's fracture
and its reduction by the Ellis plate [43]. In the three types of Smith's
fracture, internal fixation was considered.

Type 1 was treated equally well with plastic or internal fixation.
The only indication for open reduction and fixation with the Ellis plate
was persistent anterior angulation at the fracture site despite the
external splintage. Type 2 was treated by open reduction and fixation
with the Ellis plate. The Ellis plate was not indicated for the routine
treatment of type 3 fracture.

The study and testing of former implant techniques and material
was performed in 1973. In March 1973, a preliminary report of 150 cases
on the treatment of femoral fractures by internal fixation that showed
encouraging results [44] was published. It was said that this technique
improved the results by providing stable fixation and more rapid and
complete revascularization of the femoral head made eschemic by the
fracture.

In April 1973, a study made on the long term results of femoral
head replacement [45] showed that in a study of 436 cases of replacement
of the femoral head by Austin-Moore, Thompson, Vales and Judet, prosthesis
done from 1950 to 1965 revealed best results with the Austin-Moore pros-
thesis. The Austin-Moore prosthesis performance was rated as follows:

31%   -   excellent

36%   -   good ·

25%   -   fair

8%   -   poor

Relatively few patients showed much change in the results obtained; roughly as many showed long term improvement as showed deterioration. During the same year, A. Weinstein *et al.* [3] published a paper in the Journal of Biomedical Materials Research Symposium on the clinical and metallurgical analysis of orthopedic implants. The study showed that the most significant reasons for removal were infection, corrosion and fatigue failure. The recommendation of the study was that every effort to optimize the design and materials of implants be made. The importance of quality control and the necessity for having metallurgical data made available to the medical profession to determine an implant performance was also stressed.

In 1974, N. Semlitsch published a paper in Engineering in Medicine [19] on technical progress in artificial hip joints which summarized the development of material for artificial hip joints from 1939 to 1973 and introduced the aluminium oxide ceramic material, used for the first time in 1970, and unequalled for its high resistance to abrasion. However, long term clinical results must be accumulated before the performance of this material may be properly assessed.

2.3 Conclusion

Today most surgical implants are made from type 316 stainless steel, cobalt-chromium-molybdenum alloy, and titanium (Table I). Although the results obtained from these materials are generally adequate, there remains a low but persistent incidence of failure [7]. The term "failure" may be applied equally to mechanical failure or to an implant which must be removed from a patient because corrosion products can no longer be tolerated. Potentio-methods in in vivo studies were carried out, with titanium and cobalt-chromium-nickel alloys giving the best results.

The conclusion is that detailed metallurgical and corrosion studies cannot always be relied upon to provide a full account of a particular failure. Knowledge must be taken of the clinical and manufacturing details to improve implant performances. It is, therefore, essential that the fullest cooperation is maintained between surgeons, manufacturers, and specialists in materials.

TABLE I

Composition of Metallic Surgical Implant Materials [1]

Alloy	Element (wt %)									
	Cr	Ni	Fe	Mo	Co	Ti	Al	V	C	W
Stainless Steel (Grade A)	17-20	12-14	Balance	2-4	-	-	-	-	.08 (max)	-
Stainless Steel (Grade B)	17-24	12-14	Balance	2-4	-	-	-	-	.03 (max)	-
Cast Cobalt-Chromium	27-30	2.5	0.75	5-7	Balance	-	-	-	.35 (max)	-
Wrought Cobalt-Chromium	19-21	9-11	3.0 (max)	-	Balance	-	-	-	.05-.15	14-16
Analloyed Titanium	-	-	-	-	-	99	-	-	-	-
Titanium-6Al-4V	-	-	0.25 (max)	-	-	Balance	5.5-6.5	3.5-4.5	.08 (max)	-

CHAPTER 3

EXPERIMENTAL

3.1 Alloy Preparation

Approximately 500 gm of alloy were melted in an induction furnace with an Argon atmosphere and cast into an ingot about 125 mm long and 20 mm diameter. The nominal composition of the ingot and the material purity is given in Table II. After casting, the ingots were hot swaged at $1100^{\circ}C$ to the appropriate diameter for the particular test. Following swaging, the material was solution heat treated at $1250^{\circ}C$ for 4 hours in a double silica tube filled with argon and then quenched in ice water. The specimens were then machined to the appropriate shapes and dimensions. Following machining, the specimens were given a precipitation heat treatment at $800^{\circ}C$ for ten hours, the conditions for attaining maximum strength [8]. The specimens were given a final polishing with 600 grit emery paper immediately prior to testing.

3.2 Static Strength

Duplicate cylindrical tensile specimens with a gauge length of 20 mm and diameter of 3.4 mm were tested in tension on an Instron testing machine. The initial strain rate was 4×10^{-4} sec^{-1}.

3.3 Fatigue Strength

Cylindrical fatigue specimens with a gauge length of 14 mm and a gauge diameter of 3.5 mm were tested to failure on an Amsler High

TABLE II

Nominal Composition and Material Purity for Co-Ni-Cr-Ti Alloy

Element	Weight %	Atomic %	Purity
Cobalt	40	41.2	99.99
Nickel	37	38.2	99.99
Chromium	18	16.4	99.99
Titanium	5	4.2	99.70

Frequency Vibraphone with a cyclic frequency of about 100 cps. The specimens were axially loaded and most tests were conducted with loading from zero to peak tensile stress (stress ratio, R = 0). A few tests were conducted with a stress ratio of R = -1 (equal compressive and tensile stresses). The peak stresses utilized were in the range 500 MN/m^2 - 725 MN/m^2.

3.4 In-Vitro Corrosion Testing

Cylindrical specimens, 8 mm in diameter and 25 mm in length, attached to the ASTM electrode holder[9] were used for the in-vitro corrosion tests. The electrolyte used in all in-vitro corrosion tests was Ringer's solution (Table III) prepared such that the ionic concentration of the major elements was similar to that of extracellular fluid (Table III), the environment in which an actual implant is immersed. The electrolyte was prepared from a stock solution of five times concentration from which one litre of Ringer's solution was prepared by appropriate dulution immediately prior to testing. All in-vitro corrosion tests were performed in an electrochemical cell similar in design to that recommended by the ASTM [9]. All tests were conducted at $37^{o}C \pm 1^{o}C$ maintained by immersing the cell in a temperature regulated water bath and at a pH of 7.2-7.4 maintained by addition of 1N HCl or 1N NaOH.

The amount of dissolved O_2 and CO_2 gases in extracellular fluid can vary considerably in the vicinity of an implant, particularly in crevices formed between screws and plates. Therefore, in-vitro tests were conducted in several solutions containing various amounts of dissolved

TABLE III

Compositions of Ringer's Solution and Extracellular Fluid

Ringer's Solution [10]

Compound	Concentration (mg/litre)
Na Cl	6,300
Na H CO_3	2,440
K Cl	374
Mg Cl_2 · $6H_2O$	203
Mg SO_4 · $7H_2O$	123
Na_2 H PO_4	71
Na H_2 PO_4 · H_2O	69

Extracellular Fluid [11]

Element	Composition	
	mg/litre	m Eg./litre
Na+	3,266	142
K+	145	5
Cl-	3,605	103
H CO_3^-	1,708	28
Ca++	200	5
Mg++	72	3

gases as indicated in Table IV maintained by bubbling controlled amounts of O_2, CO_2 and Argon through the solution. A Radiometer acid-base analyzer, type PHM 71 was used to measure the O_2, CO_2 concentrations and the pH.

Three types of in-vitro corrosion tests were performed. Cathodic and linear anodic polarization studies to obtain an indication of the corrosion rate of the alloy [12] and cyclic anodic polarization to determine values of rest potential, E_R, pitting potential, E_c, and protection potential, E_p.

a) Cathodic Polarization

Cathodic polarization studies were conducted by passing a cathodic current from a Kiethly Constant Current Source, model #225, between the specimen and the platinum counter electrodes. The current densities were in the range 0 - 10 $\mu A/cm^2$ and the system was allowed to stabilize for 5 minutes at each value of current density before the value of potential was measured with respect to a saturated calomel electrode using a Kiethly Digital Multimeter, model #160.

b) Linear Anodic Polarization

These tests were conducted in a similar manner to those for cathodic polarization except that small anodic current densities (0 - 2 $\mu A/cm^2$) were utilized so that the potential change from the rest potential was linear with current density and in the order of 10 mv.

c) Cyclic Anodic Polarization

Cyclic potentiodynamic anodic polarization curves at a scan rate of 600 mv/hour were obtained using a Wenking Potentiostat, model #68TS3,

TABLE IV

O_2 and CO_2 Concentrations for In-Vitro Corrosion Tests

Designation	Concentration (mm Hg)	Designation	Concentration (mm Hg)
Low CO_2	<8	Low O_2	<10
Medium CO_2	40-60	Medium O_2	80-120
High CO_2	90-110	High O_2	250-300

TABLE V

Tensile Properties of Co-Ni-Cr-Ti Alloy

Ultimate Strength (MN/m^2)	0.2% Offset Yield Strength (MN/m^2)	Elongation (%)
954	735	19

and an Erwin Halstrup Motorpotentiometer, model #MP165. A schematic of the circuitry is shown in Figure 1. All runs were conducted in duplicate. The current was monitored continuously via the potentiostat recorder terminals using a Rikadenki, model #B-104, strip chart recorder. The potential scan was reversed when the current density reached a value about 2 orders of magnitude greater than the current density at the pitting or breakdown potential.

3.5 In-Vivo Corrosion Testing

Cylindrical specimens about 4 mm in length and 3 mm in diameter were accurately weighed on a Sartorius microbalance which weighs to 10^{-5} grams and implanted in the thigh tissues of three month old New Zealand white rabbits. Some control specimens of type 316L stainless steel were also implanted in the opposite thigh. The animals were sacrificed at implantation times from 6 - 17 months and the pellets removed, cleaned and weighed. Samples of surrounding tissue were also removed for pathological examination.
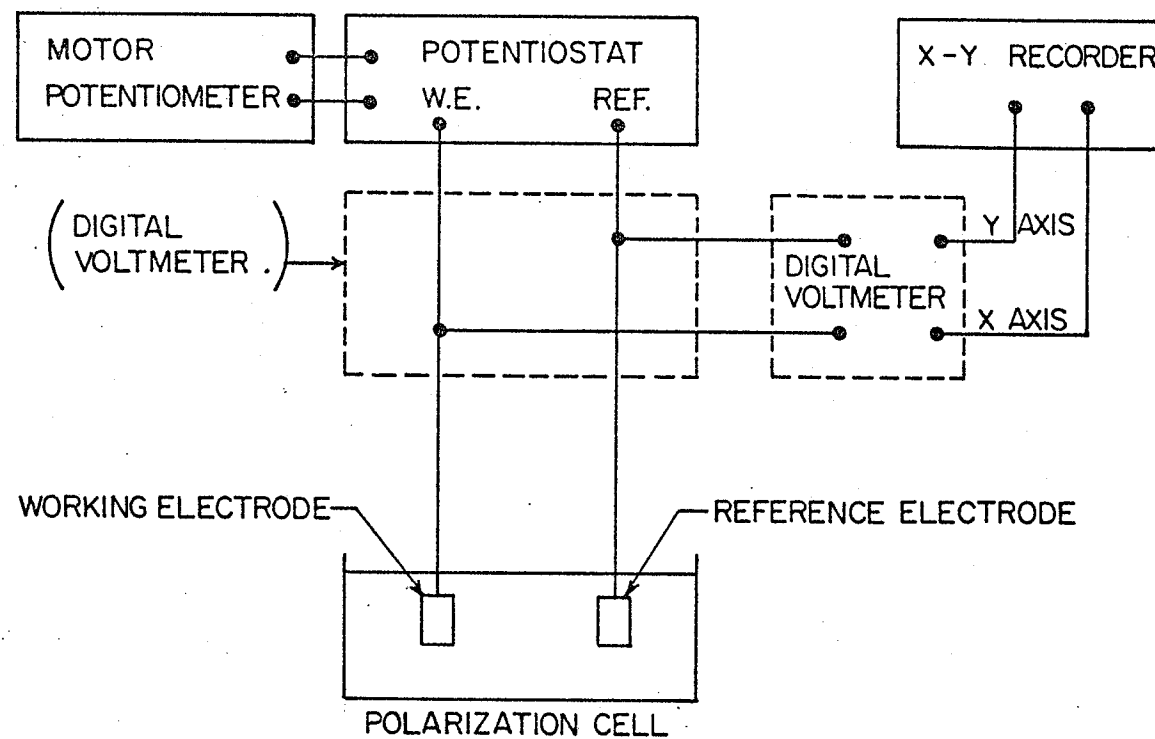
SCHEMATIC CIRCUITRY FOR POTENTIODYNAMIC POLARIZATION

Fig. I

CHAPTER 4

RESULTS

4.1 Static Strength

The tensile properties of the duplicate specimens were virtually identical and are given in Table V (see Page 22).

4.2 Fatigue Strength

The fatigue life for the Co-Ni-Cr-Ti alloy at various peak stress levels is given in Table VI for a stress ratio R = 0 and Table VII for R = -1. The S-N curves are compared with that for annealed stainless steel in Fig. 2.

4.3 In-Vitro Corrosion Testing

a) Cathodic Polarization

An estimate of the corrosion current density can be obtained by Tafel extrapolation of the linear portion of the cathodic polarization curve to the rest potential, E_R [12]. Cathodic polarization curves for three O_2 and CO_2 concentrations are given in Fig. 3 and the results are summarized in Table VIII.

b) Linear Anodic Polarization

The linear anodic polarization curves for three O_2 and CO_2 concentrations are shown in Fig. 4. The corrosion current can be estimated from the slope (polarization resistance) of the linear anodic polarization curve using the relation [12]:
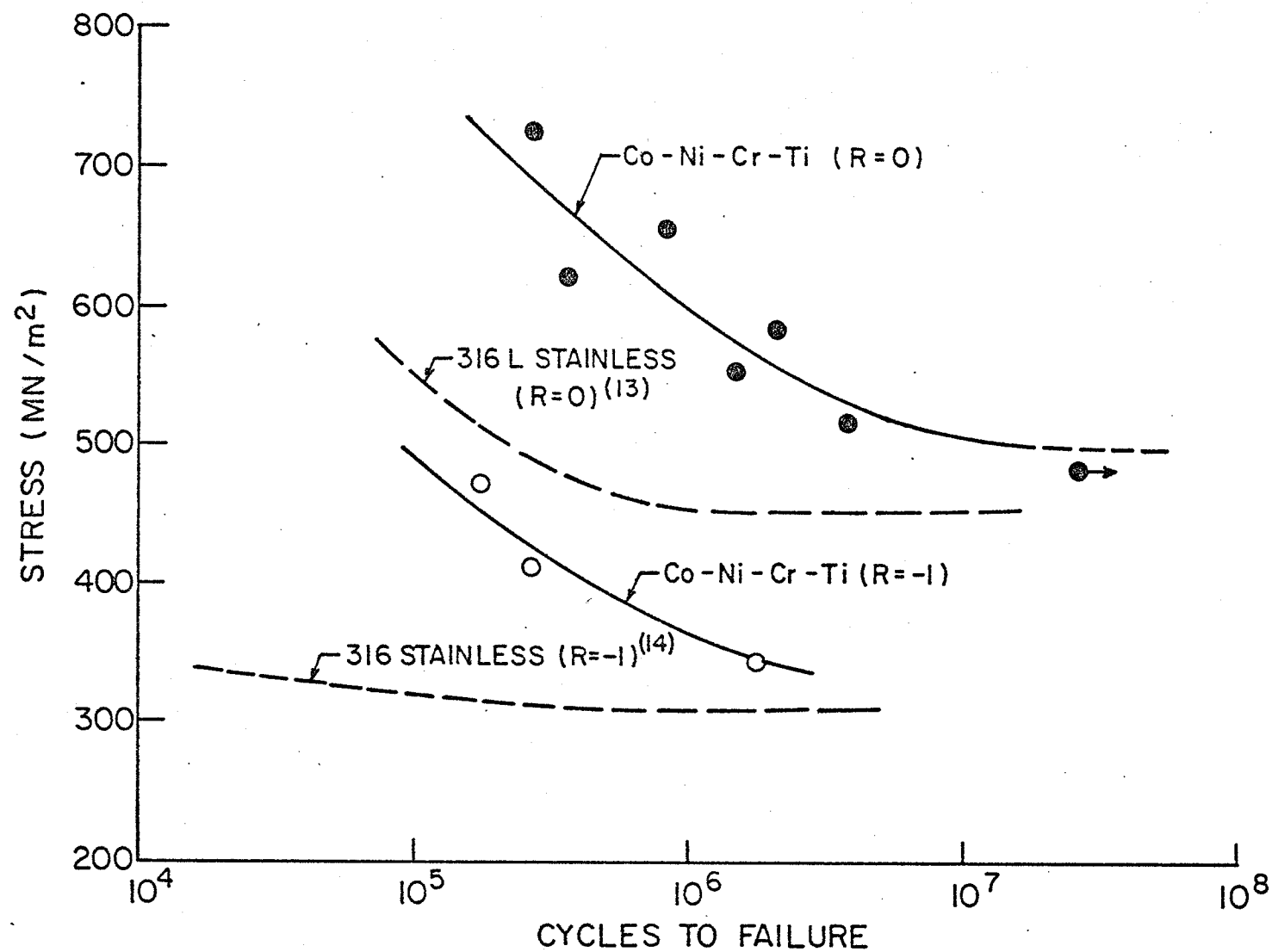
Fig. 2

TABLE VI

Fatigue Life of Co-Ni-Cr-Ti Alloy at Stress Ratio R = 0

Peak Stress (MN/m^2)	Fatigue Life (Cycles)
483	2.6×10^7 (did not fail)
518	3.8×10^6
552	1.5×10^6
587	2.1×10^6
621	3.9×10^5
656	8.3×10^5
725	2.9×10^5

TABLE VII

Fatigue Life of Co-Ni-Cr-Ti Alloy at Stress Ratio R = -1

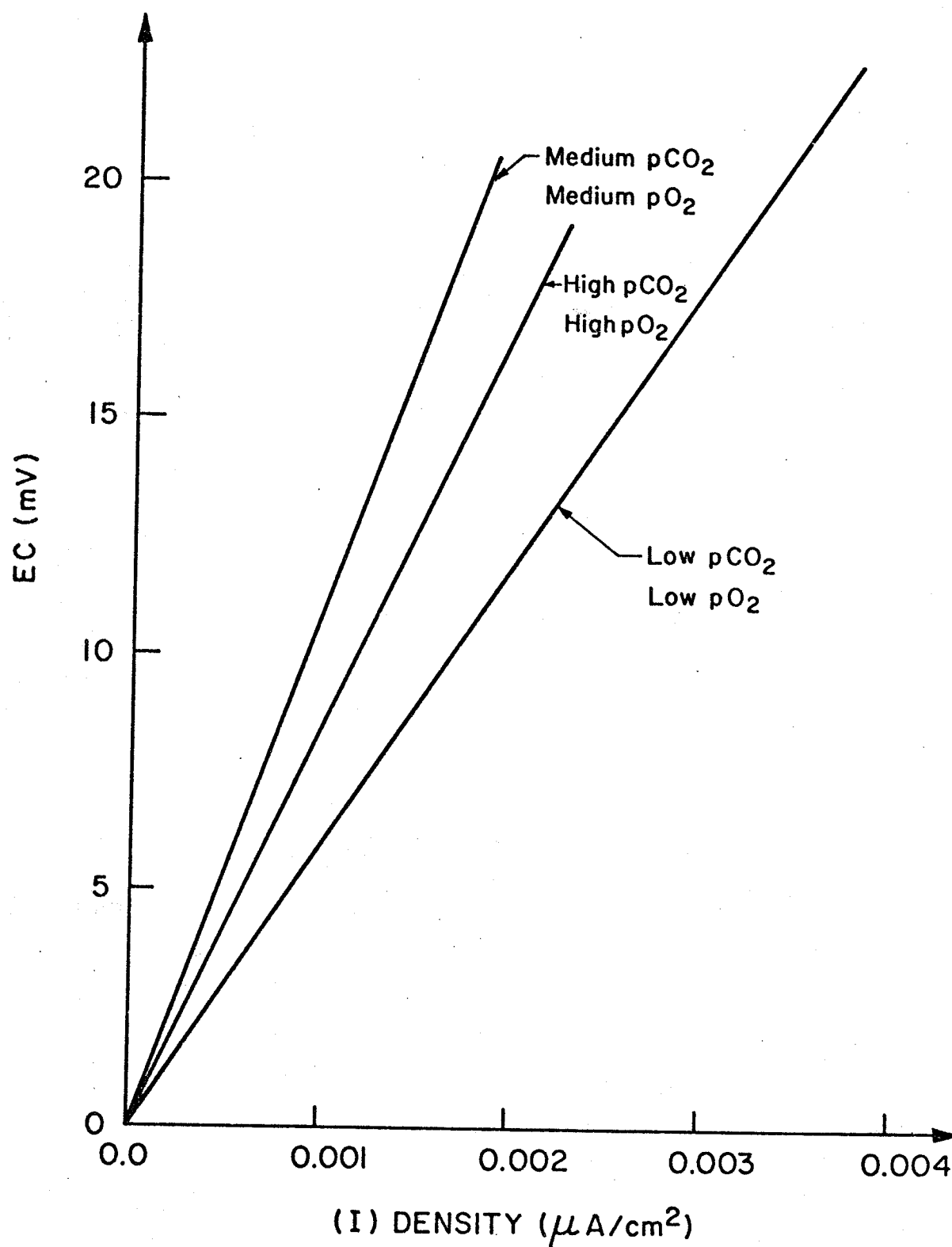| Peak Stress (MN/m^2)	Fatigue Life (Cycles)
345	1.7×10^6
414	2.7×10^5
483	1.8×10^5

Fig. 3 . ANODIC POLARIZATION Co−Ni−Cr−Ti .

TABLE VIII

Cathodic and Linear Polarization Results Co-Ni-Cr-Ti Alloy

O_2 Concentration	CO_2 Concentration	Cathodic Tafel Slope (V/decade)	Corrosion Current Tafel Extrapolation ($\mu A/cm^2$)	Polarization Resistance (V/μ A/cm^2)	Corrosion Current from Eq. [2] ($\mu A/cm^2$)
Low	Low	.310	1.07×10^{-2}	7	1.9×10^{-2}
Medium	Medium	.230	4.2×10^{-3}	11	4.2×10^{-3}
High	High	.230	1.3×10^{-2}	8	1.4×10^{-2}

$$I_{corr} = \frac{B_a \, B_c}{2.3 \, (B_a + B_c)(\Delta E / \Delta I)} \qquad (1)$$

where I_{corr} = corrosion current density

$\quad\quad B_a$ = anodic Tafel slope (volts/decade of current)

$\quad\quad B_c$ = cathodic Tafel slope (volts/decade of current)

$\quad\quad \frac{\Delta E}{\Delta I}$ = slope of the linear anodic polarization curve

The rest potential of the Co-Ni-Cr-Ti alloy lies in a passive region where the anodic Tafel slope, B_a , is very large (see Fig. 7) and therefore if B_a approaches infinity, Eq. (1) reduces to:

$$I_{corr} \approx \frac{B_c}{2.3 \, (\Delta E / \Delta I)} . \qquad (2)$$

The cathode Tafel slopes, B_c , obtained from Fig. 4, the polarization resistance, $\Delta E / \Delta I$, and the corrosion current, I_{corr}, calculated from Eq. (2) are given in Table VIII.

c) Cyclic Anodic Polarization

Cyclic anodic polarization curves were obtained in duplicate for various CO_2 and O_2 concentrations. These polarization curves (Figures 5 - 13) show the values of rest or corrosion potential, E_R, pitting or breakdown potential, E_c, and protection potential, E_p. The protection potential, E_p, is defined as the potential at which, on the return voltage scan, the current density equals that on the forward scan. In the cases where the protection potential is lower (more active) than the rest potential, E_R, the protection potential, E_p, is defined as the potential at which the current density became cathodic on the return
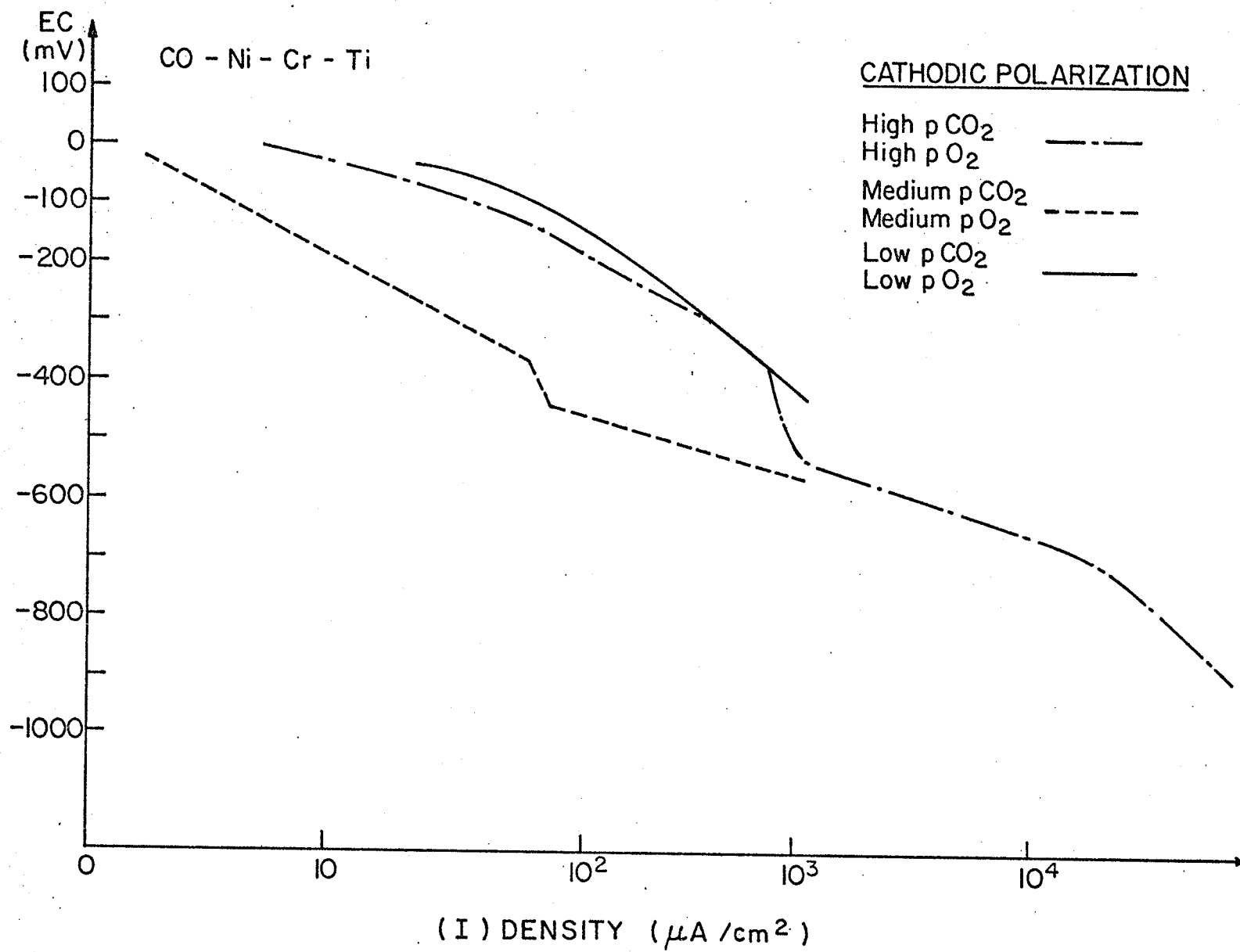
Fig. 4

Fig. 5 Cyclical Potentiodynamic Scan.
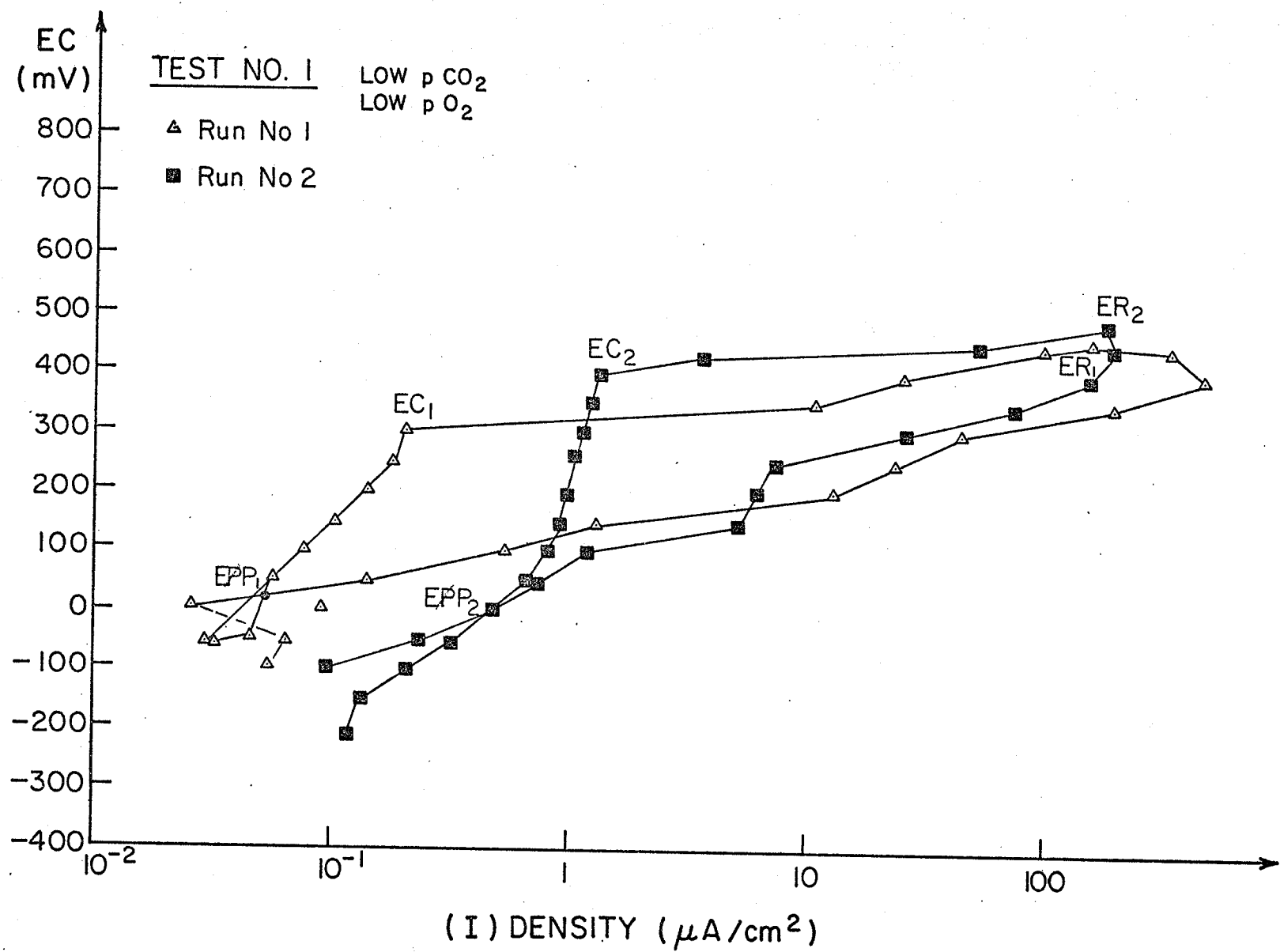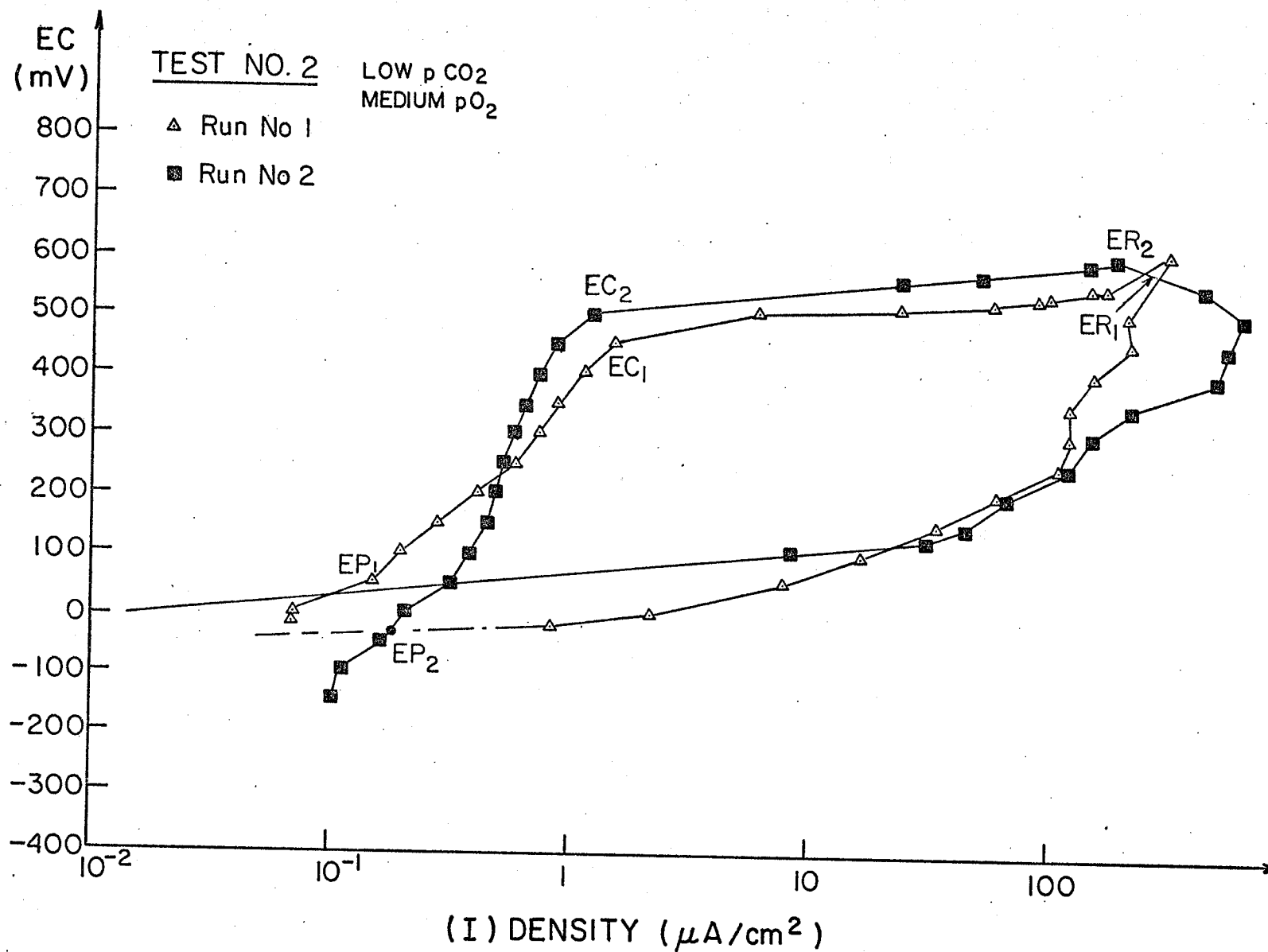
Fig. 6 Cyclical Potentiodynamic Scan.
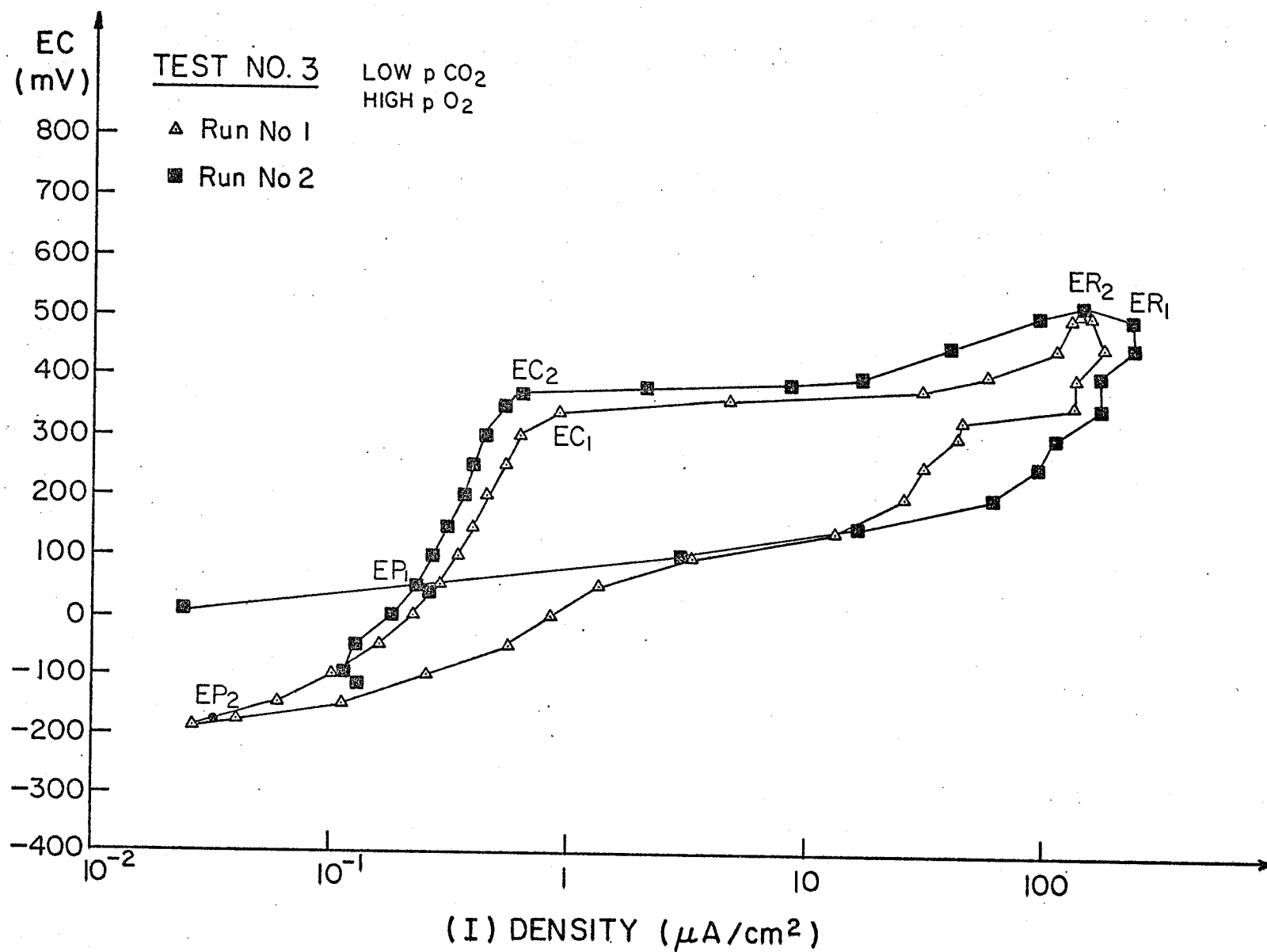
33.

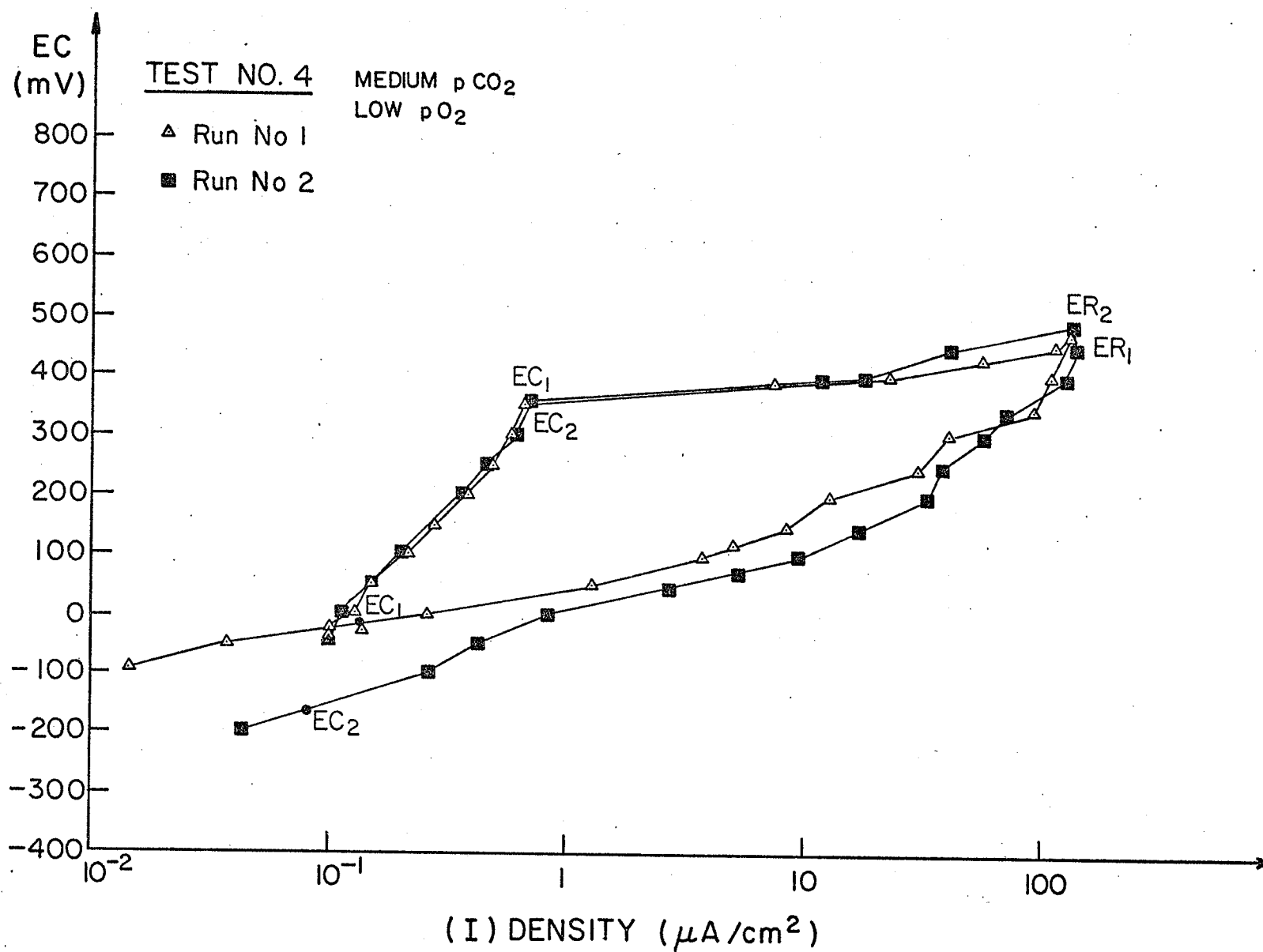Fig. 7 Cyclical Potentiodynamic Scan.

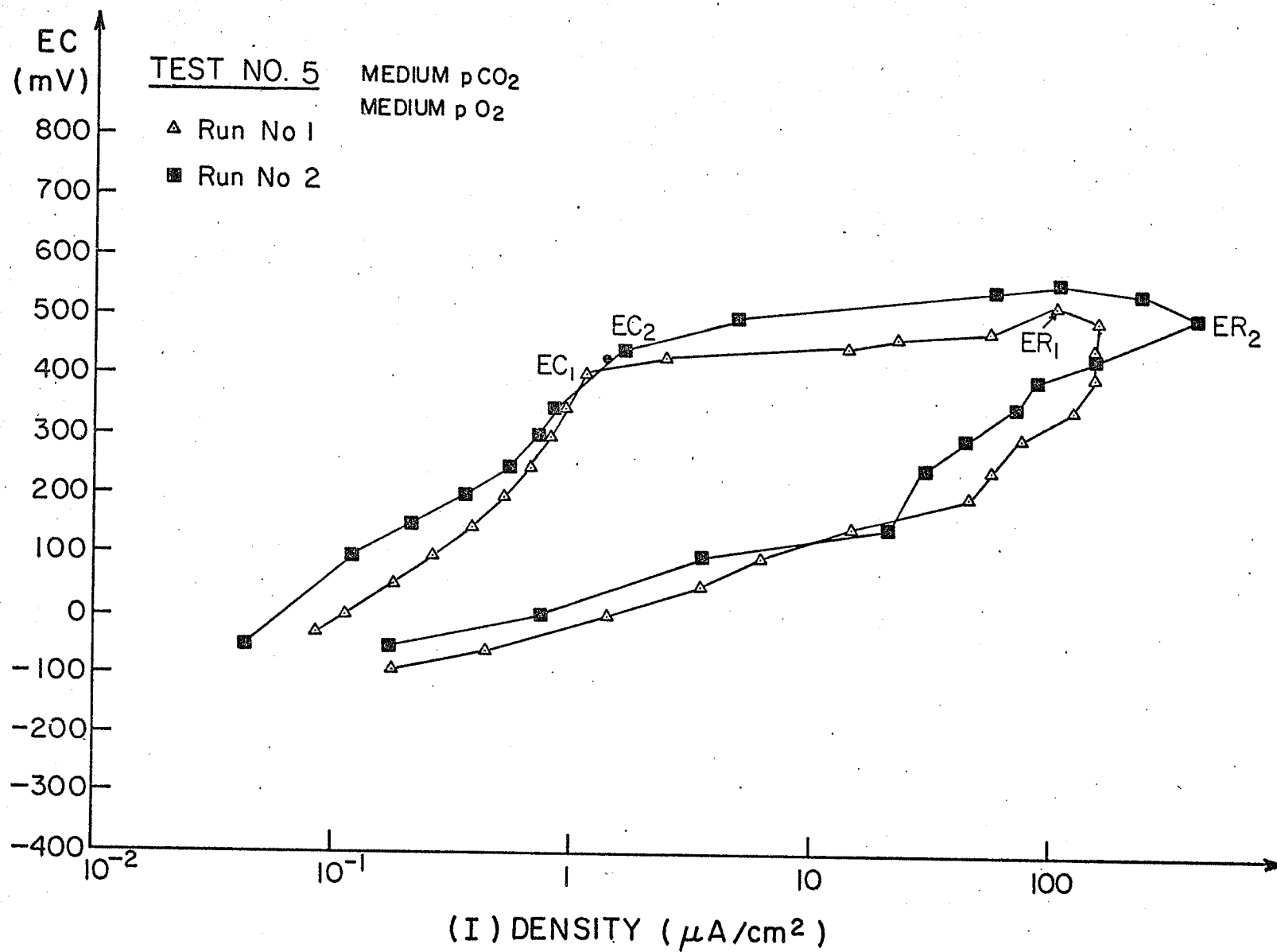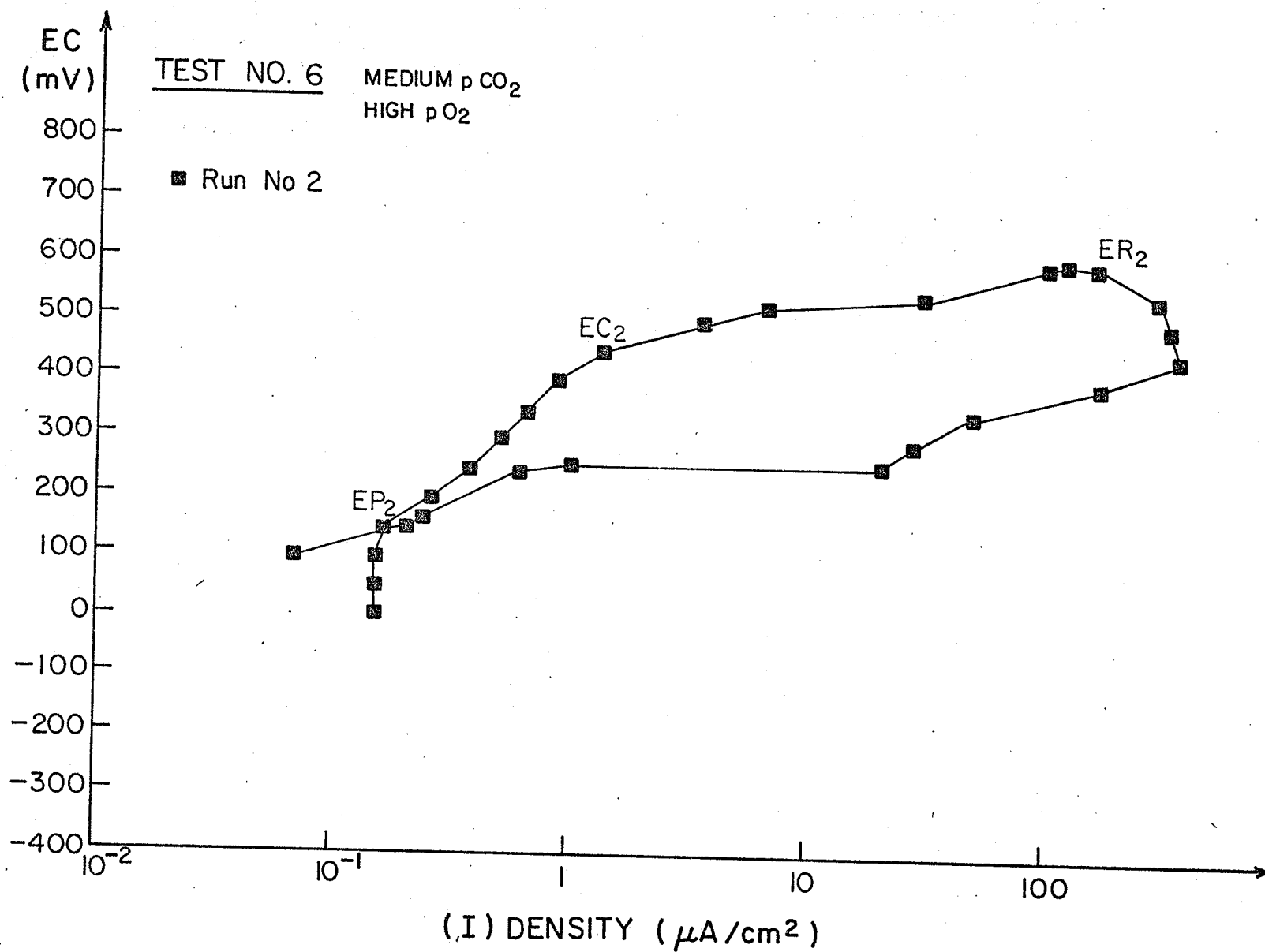Fig. 8 Cyclical Potentiodynamic Scan.

Fig. 9 Cyclical Potentiodynamic Scan.

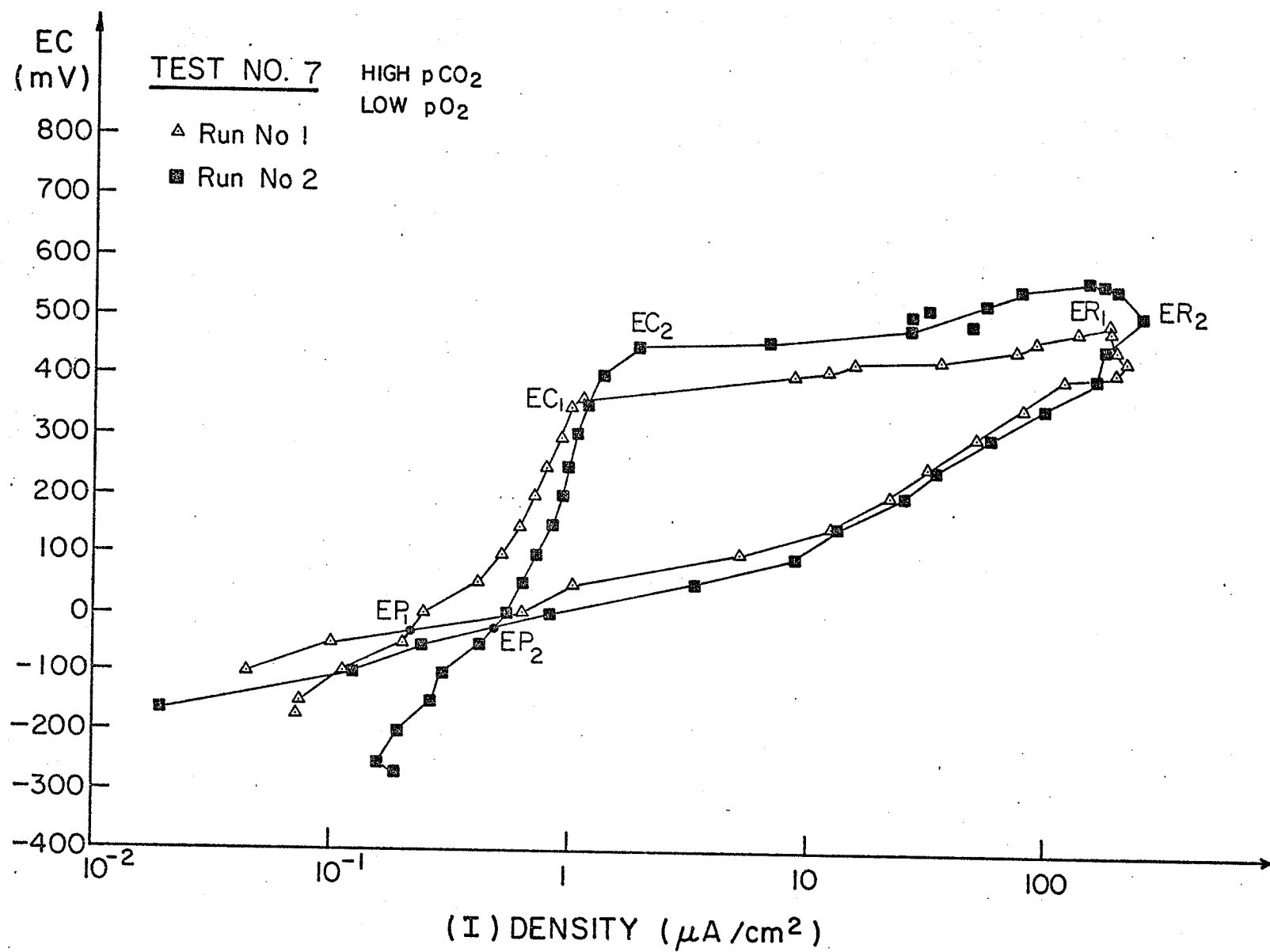Fig. 10 Cyclical Potentiodynamic Scan.

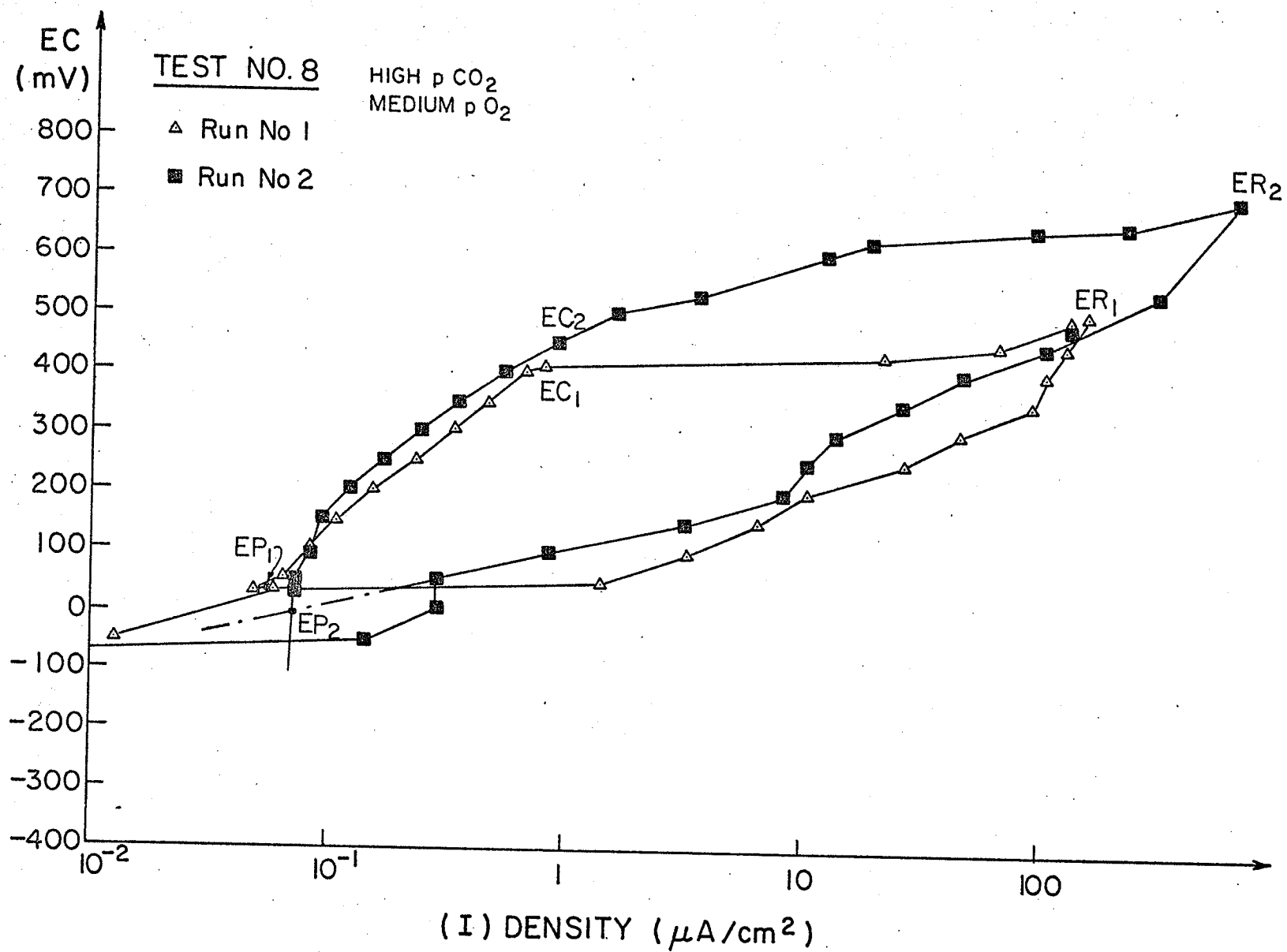Fig. 11
Cyclical Potentiodynamic Scan.

38.

Fig. 12 Cyclical Potentiodynamic Scan.
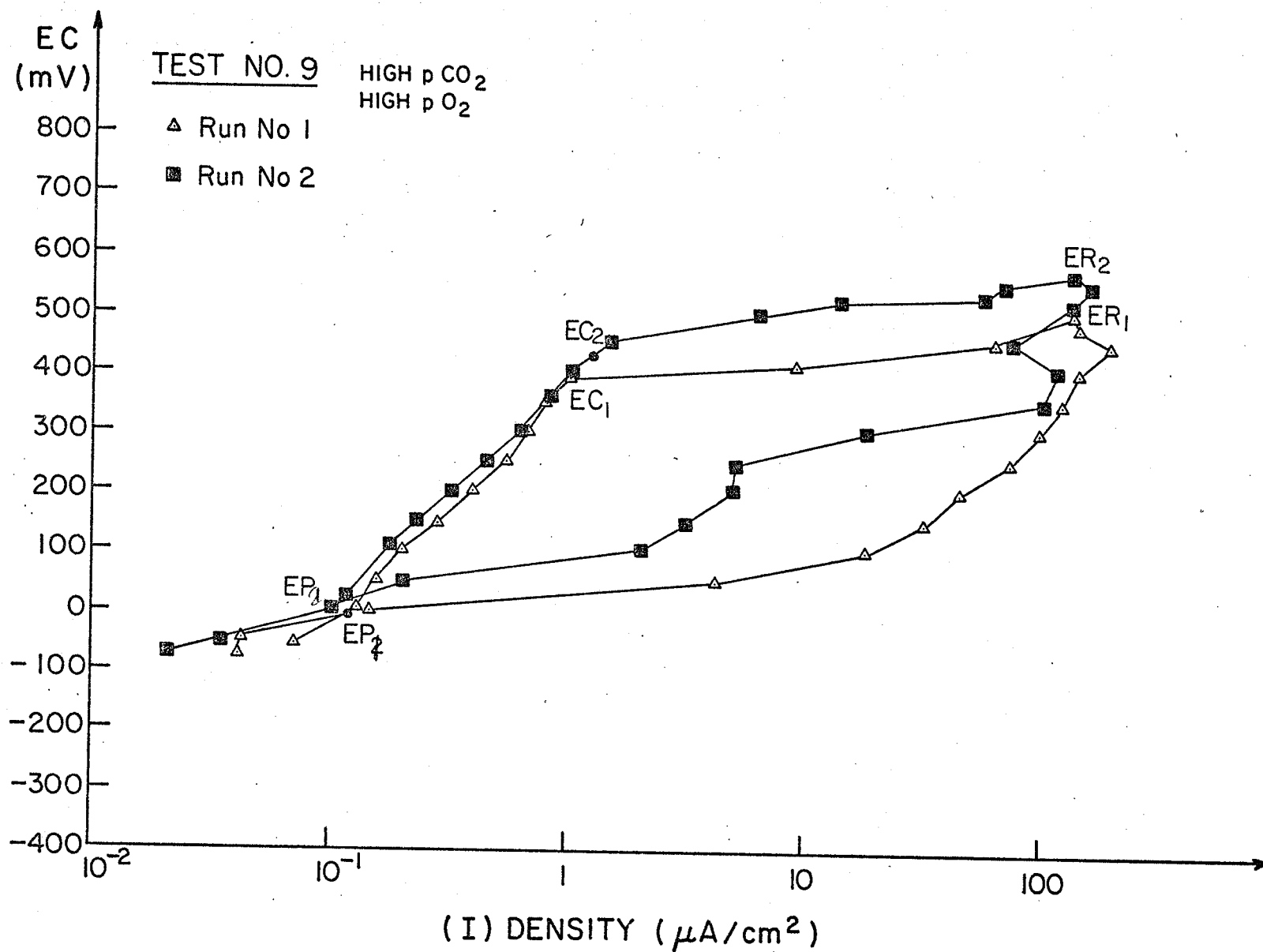
Fig. 13
Cyclical Potentiodynamic Scan.

40.

scan. The results for the polarization curves obtained at various CO_2 and O_2 concentrations are summarized in Table IX and in Figs. 5 - 13. The values obtained for E_R, E_c and E_p in Table IX generally agreed to within $\pm$ 25 m.v. for the duplicate runs. The values given for E_c - E_p and E_c - E_R are therefore likely accurate to $\pm$ 50 m.v.

4.4 In-Vivo Corrosion Studies

The corrosion data for the Co-Ni-Cr-Ti alloy implants and the type 316 L stainless steel control implants are given in Table X. All pellets were shiny upon removal with no evidence of corrosion or pitting. The pathological studies of adjacent tissue showed no adverse tissue reaction for either Co-Ni-Cr-Ti or stainless steel implants. A typical pathological report follows:

"An irregular fragment of firm, resiliant, translucent white tissue measuring 2.5 x 1 x 1.3 cm was received. Embedded within it was a smooth, glistening metal pellet measuring 0.4 cm in diameter and 0.35 cm in length. The walls of the cavity in which the pellet was embedded were smooth and glistening.

The thin capsule which surrounded the cylindrical metal pellet consisted of a thin layer of avascular fibrous tissue approximately 16 microns in thickness. No inflammatory or reactive change was evident in the adjacent adipose tissue or muscle."

Because of the inherent inaccuracies involved in weight loss experiments, the values given in Table X are quite subjective but they do indicate that the corrosion rate is very small.

TABLE IX

Summary of Cyclic Anodic Polarization Results on Co-Ni-Cr-Ti Alloy

O_2 and CO_2 Concentrations	Rest Potential E_R (mv vs. S.C.E.)	Breakdown Potential E_c (mv vs. S.C.E.)	Protection Potential E_p (mv vs. S.C.E.)	$E_c - E_p$ (m.v.)	$E_c - E_R$ (m.v.)
Low CO_2 Low O_2	-132	350	+10	340	482
Low CO_2 Medium O_2	-82	450	-3	453	535
Low CO_2 High O_2	-154	355	-90	450	604
Medium CO_2 Low O_2	-38	355	-90	455	483
Medium CO_2 Medium O_2	-69	423	-101	524	593
Medium CO_2 High O_2	-18	400	-40	440	458
High CO_2 Low O_2	-176	395	-12	407	583
High O_2 Medium O_2	+30	430	+7	423	453
High CO_2 High O_2	-39	400	-1	401	440

TABLE X

Results of In-Vivo Corrosion Studies on Co-Ni-Cr-Ti Alloy

Implant Alloy	Duration of Implantation (Days)	Weight Upon Implantation (gms)	Weight Upon Removal (gms)	Weight Loss (gms)
Co-Ni-Cr-Ti	170	0.48495	0.48495	0
Co-Ni-Cr-Ti	189	0.51624	0.51624	0
Co-Ni-Cr-Ti	439	0.43606	0.43600	6×10^{-5}
Co-Ni-Cr-Ti	469	0.50846	0.50842	4×10^{-5}
Type 316 L Stainless Steel	170	0.34565	0.34565	0
Type 316 L Stainless Steel	189	0.41378	0.41378	0
Type 316 L Stainless Steel	469	0.38488	0.38481	7×10^{-5}

CHAPTER V

DISCUSSION

5.1 Discussion

The tensile properties of the Co-Ni-Cr-Ti alloy (Table v) exceed the minimum ASTM requirements of 896 MN/m^2 ultimate strength and 379 MN/m^2 yield strength for wrought cobalt-chromium alloys [1]. No ductility limits are specified in the ASTM standard for wrought cobalt-chromium alloys but the elongation of 19% greatly exceeds the 8% minimum specified for cast cobalt-chromium-molybdenum alloys [1]. No fatigue strength data are included in the ASTM specifications but the fatigue strength of the Co-Ni-Cr-Ti alloy exceeds that of type 316 L stainless steel as shown in Fig. 1. Therefore, the Co-Ni-Cr-Ti alloy likely has sufficient strength for use as a surgical implant material.

Corrosion rates for the Co-Ni-Cr-Ti alloy can be estimated from the corrosion currents given in Table VIII and Faraday's laws of electrolysis. The corrosion rate can be calculated from:

$$R = \frac{W \times I_{corr} \times A}{V \times 96,500}$$

where R   = corrosion rate (gms/sec)

W   = atomic weight

I_{corr} = corrosion current density (amps/cm^2)

A   = surface area (cm^2)

V   = valence of metal

The atomic weight, W , of the Co-Ni-Cr-Ti alloy can be calculated as 52.2 gms/mole from the data in Table II, the corrosion current is approximately 10^{-8} amps/cm^2 from Table VIII, the surface area of the implanted specimens is about 0.5 cm^2, and the valence is approximately 2 since both cobalt and nickel have this value.

The calculated corrosion rate for the implanted specimens is therefore:

$$R = \frac{52 \times 10^{-8} \times 0.5}{2 \times 96,500} \simeq 1.4 \times 10^{-12} \text{ gms/sec}$$

For an implantation time of 469 days the calculated corrosion loss is therefore about 5×10^{-5} gms. This value is essentially identical with the actual measured values for implanted specimens (Table X). Because of the inherent inaccuracies in measuring the very small weight losses involved, the agreement between the calculated and experimental results may be largely fortuitous. However, it is clear that the corrosion rate of the Co-Ni-Cr-Ti alloy is very low and certainly not appreciably greater than that of present surgical implant materials.

The potentiodynamic anodic polarization results (Table IX) indicate that the rest or corrosion potential of the alloy is in the order of -50 mv vs S.C.E. and the breakdown or pitting potential, E_c , is over 440 m.v. higher (more noble) than the rest potential with the concentrations of CO_2 and O_2 in solution having no consistent effect on the values of any of the potentials.

It is known that the breakdown potential of an implant alloy must be substantially above (more noble than) the rest or corrosion

potential in order to avoid pitting corrosion during service but the minimum value of E_c - E_R which prevents pitting corrosion is not known. However, pitting corrosion has been known to occur in austenitic stainless steel implants [2] where the breakdown potential is about 350 mv more noble than the rest potential [5,10] (tested under the same conditions as the Co-Ni-Cr-Ti alloy) and therefore the value of 350 mv would seem to be about the minimum acceptable value for the separation between the corrosion and breakdown potentials. The separation of 440 mv for the Co-Ni-Cr-Ti alloy would therefore appear to be adequate for surgical implant applications.

The severity of, or susceptibility to, crevice corrosion of an alloy has been shown to be related to the nobility of the protection potential, E_p, or, more exactly, the magnitude of the difference between the breakdown and protection potentials [15,16], with the severity or susceptibility increasing with an increase in the difference between the breakdown and protection potentials. Again, a minimum value for the difference between breakdown and protection potentials to render a material immune to crevice corrosion has not been established but Cobalt-Chromium alloys which are relatively, but not completely, immune to crevice corrosion [3] in surgical implant applications have a difference potential of about 100 mv [10]. On the other hand, austenitic stainless steel which is very prone to crevice corrosion [3,4] has a difference potential of about 400 mv [10]. Therefore, it would appear that a difference potential of about 100 mv is the maximum allowable to render an implant alloy relatively immune to crevice corrosion.

The cyclic anodic polarization results for the Co-Ni-Cr-Ti alloy (Table IX) show the value of protection potential for this alloy is quite active resulting in a large difference potential, $E_c - E_p$, of about 400 mv, very similar to the value obtained for austenitic stainless steel tested under similar conditions [5,10]. It is suggested, therefore, that the Co-Ni-Cr-Ti alloy would suffer from crevice corrosion in multi-component implants to about the same degree as those manufactured from austenitic stainless steel. However, in vivo studies would have to be performed to substantiate this.

The strength and corrosion tests indicate that the Co-Ni-Cr-Ti precipitation hardening alloy has equivalent or superior properties compared with present implant materials. Being a wrought alloy and having good ductility the problems of porosity and low ductility evident in some casting alloys are also avoided. Cyclic anodic polarization studies indicate that the alloy may, however, be susceptible to crevice corrosion to about the same degree as austenitic stainless steel. It is important to note that there appear to be no inherent difficulties with the use of precipitation hardening alloys per se for surgical implants and therefore it may be possible to introduce implant materials with much better strength and corrosion resistance than present materials. The only drawback of the Co-Ni-Cr-Ti alloy investigated in this investigation is its potential susceptibility to crevice corrosion. However, since Co-Cr alloys with little or no Ni content are relatively immune to crevice corrosion it should be possible to develop precipitation hardening alloys which contain little or no Ni and thereby obtain an alloy

which has high strength, good general corrosion resistance, and good
resistance to crevice corrosion as well.

CHAPTER VI

CONCLUSIONS

6.1 Conclusions

Upon evaluation of the experimental data for the precipitation hardened Co-Ni-Cr-Ti alloy it is possible to draw the following conclusions concerning the suitability of a precipitationed hardened alloy for surgical implant applications:

1. The static and fatigue strengths of the alloy are equivalent or superior to those exhibited by present implant materials.

2. The corrosion resistance of the alloy with respect to corrosion current and breakdown potential is equivalent or superior to present implant materials.

3. The alloy may be susceptible to crevice corrosion in multi-component implants due to an active value of protection potential.

4. It may be possible to raise the value of the protection potential by reducing the nickel content of the alloy.

5. There appear to be no inherent difficulties in utilizing precipitation hardened alloys for surgical implant applications.

REFERENCES

[1] Annual Book of ASTM Standards - Part 46, Specifications F138, F75, F90, F67, F36 (1976).

[2] Cahoon, J.R. and Paxton, H.W., J. Biomed. Res., 2, pp. 1-22 (1968).

[3] Weinstein, A., Amstutz, H., Pavon, G. and Franceschini, V., Materials and Design Considerations for the Attachment of Prostheses to the Musculo-Skeletal System, Biomedical Materials Symposium #4, Interscience Publication, pp. 297-325 (1973).

[4] Colangelo, V.J. and Greene, W.D., J. Biomed. Mat. Res., 3, 246 (1969).

[5] Bandy, R. and Cahoon, J.R., Corrosion, 33, pp. 204-208 (1977).

[6] Semlitsch, Engineering in Medicine, 3, #4, pp. 10-19 (1974).

[7] Smethurst, Edward, University of Nottingham, Nottingham, England. Unpublished data.

[8] Chaturvedi, M.C., Lloyd, D.J. and Chung, D.W., Met. Sc., 10, pp. 373-378 (1976).

[9] Annual Book of ASTM STANDARDS: American Society for Testing and Materials, Specification G5-1972, Part 10, pp. 592-602 (1976).

[10] Cahoon, J.R., Bandyopadhya, R. and Tennese, Laura, J. Biomed. Mater. Res., Vol. 9, pp. 259-264 (1975).

[11] Guyton, Arthur C., Textbook of Medical Physiology, 4th Edition, W. B. Saunders and Co., p. 39 (1971).

[12] Fontana, M.G. and Greene, N.D., Corrosion Engineering, McGraw-Hill, New York, pp. 342-345 (1967).

[13] Holte, R.N., M.Sc. Thesis, University of Manitoba (1976).

[14] Grover, H.J., J. of Mat., Vol. 1, pp. 413-424 (1966).

[15] Wilde, R.E., Corrosion, Vol. 28, pp. 283-291 (1972).

[16] Wilde, R.E. and Williams, E., J. Electrochem. Soc., Vol. 118, pp. 1057-1062 (1971).

[17] Cahoon, J.R. and Paxton, H.W., J. Biomed. Mat. Res., 4, pp. 223-244 (1970).

[18] Cahoon, J.R. and Tennese, W.W., Med. Dev. Art. Org., 1, #4, pp. 635-645 (1973).

[19] Semlitsch, M., Eng. in Medicine, 3, #4, pp. 10 - 19 (1974).

[20] McCarroll, H.R. (M.D.), Trials and tribulations in attempted femoral lengthening", Journal of Bones and Joints Surgery, Vol. 32-A*, No. 1, pp. 132-140 (Jan. 1950).

[21] Cleveland, M. (M.D.), Bosworth, D.M. (M.D.) and Della Pietra, A. (M.D.), Subtrochanteric osteotomy and spline fixation for certain disabilities of the hip joint - A preliminary report, J. of B. & J. Surgery, Vol. 33-A, No. 2, pp. 351-361 and 395-420 (April 1951).

[22] McBride, E.D. (M.D.), A femoral-head prosthesis for the hip joint - four years experience and the results, J. of B. & J. Surgery, Vol. 34-A, No. 4, pp. 989-996 (October 1952).

[23] Laing, P.G. (M.D.), The significance of metallic transfer in the corrosion of orthopaedic screws, J. of B. & J. Surgery, Vol. 40-A, No. 4, pp. 853-869 (July 1958).

[24] Cohen, J. (M.D.) and Hammond, G. (M.D.), Corrosion in a device for fracture fixation, J. of B. & J. Surgery, Vol. 41-A, No.3, pp. 524-534 (April 1959).

[25] Laing, P.G. (M.D.), Madaney, L.R. and Grebner, M.A., A radioisotopic investigation of the contamination of screws and tissues by screwdrivers - A study in applied metallurgy, J. of B. & J. Surgery, Vol. 41-A, No. 3, pp. 535-545 (April 1959).

[26] Ferguson, A.B. Jr. (M.D.), Laing, P.G.(M.D., F.R.C.S.) and Hodge, E.S. (Ph.D.), The ionization of metal implants in living tissues, J. of B. & J. Surgery, Vol. 42-A, No. 1, pp. 77-90 (January 1960).

[27] Cohen, J. (M.D.) and Foultz, W. Sanford (M.D.), Failure by corrosion of a Steinmann pin used for intramedullary fixation, J. of B.& J. Surgery, Vol. 42-A, No. 7, pp. 1201-1206 (October 1960)

[28] Hicks, J. and Cater, W.H., Minor reactions due to modern metal, J. of B. & J. Surgery, Vol. 44-B**, No. 1, pp. 122-128 (February 1962).

[29] Cohen, J. (M.D.), Corrosion testing of orthopaedic implants, J. of B. & J. Surgery, Vol. 44-A, No. 2, pp. 307-316 (March 1962).

[30] Ferguson, A.B. (M.D.), Akahoshi, Y. (M.D.), Laing, P.G. (M.B.,B.S.) and Hodge, E.S. (Ph.D.), Characteristics of trace ions released from embedded metal implants in the rabbit, J. of B. & J. Surgery, Vol. 44-A, No. 2, pp. 323-336 (March 1962).

* American Edition   ** British Edition

[31] Charnley, J., The bonding of prostheses to bone by cement, J. of
      B. & J. Surgery, Vol. 46-B, No. 3, pp. 518-529 (August 1964)

[32] Scales, J.T., The development of British standards for Surgical
      implants, J. of B. & J. Surgery, Volume 47-B, No. 1, pp. 111-117
      (February 1965).

[33] Burrows, H. Jackson, Pitfalls in major prosthetic replacement of
      bone, Proceedings and reports of councils and associations,
      J. of B. & J. Surgery, Vol. 49-B, No. 2, p. 387 (May 1967).

[34] Heywood-Waddington, M.B., Use of the Austin Moore prosthesis for
      advanced osteoarthritis of the hip, J. of B. & J. Surgery,
      Vol. 48-B, No. 2, pp. 236-244 (May 1962).

[35] Law, W.A. (O.B.E.,M.D.), Late results in vitallium-mold arthroplasty
      of the hip, J. of B. & J. Surgery, Vol. 44-A, No. 8, pp. 1497-1517,
      (Dec. 1962).

[36] Mears, D.C., Electron-probe microanalysis of tissue and cells from
      implant areas, J. of B. & J. Surgery, Vol. 48-B, No. 3,
      pp. 567-576 (August 1966).

[37] Ferguson, A.B. Jr. (M.D.), Laing, P.G. (M.B.,F.R.C.S.) and
      Hodge, E.S. (Ph.D.), The ionization of metal implants in living
      tissues, J. of B. & J. Surgery, Vol. 42-A, No. 1, pp. 77-90
      (January 1960).

[38] Pappas, A.M. (M.D.) and Cohen, J. (M.D.), Toxicity of metal particles
      in tissue culture - Part I: A new assay method using cell counts
      in the phase of replication, J. of B. & J. Surgery, Vol. 50-A,
      No. 3, pp. 535-546 (April 1968).

[39] Mital, M. (M.D.) and Cohen, J. (M.D.), Toxicity of metal particles
      in tissue culture - Part II: A new assay method using cell counts
      in the lag phase, J. of B. & J. Surgery, Vol. 50-A, No. 3,
      pp. 547-556 (April 1968)

[40] Girzadas, D.V. (M.D.), Greens, S. (M.D.), Clayton, M.C. (M.D.) and
      Leidholt, J.D. (M.D.), Performance of a hinged metal knee pros-
      thesis, J. of B. & J. Surgery, Vol. 50-A, No. 2, pp. 355-364
      (March 1968).

[41] Homsy, C.A. (M.D.), Stanley, R.F. (M.D.), Anderson, M.S. (M.D.) and
      King, J.W. (M.D.), Reduction of tissues and bone adhesion to
      cobalt alloy fixation appliances - Proceedings of the thirty-
      third annual meeting of the Western Orthopedic Association,
      J. of B. & J. Surgery, Vol. 52-A, No. 6, pp. 1269   (Sept. 1970).

[42] Galante, J.O. (M.D.), Rostoker, W. (M.D.), Lueck, R. (M.D.) and
         Ray, R.D. (M.D.), Sintered fiber metal composites as a basis
         for attachment of implant to bone - Proceedings of the thirty-
         seventh Annual Meeting of the American Academy of Orthopaedic
         Surgeons, J. of B. & J. Surgery - Vol. 52-A, No. 4, pp. 814-
         (June 1970).

[43] Fuller, D.J. (M.D.), The Ellis plate operation for Smith's fracture,
         J. of B. & J. Surgery, Vol. 55-B, No. 1, pp. 173-178 (Feb. 1973).

[44] Meyers, M.H. (M.D.), Harvey, J.P. Jr. (M.D.) and Moore, T.M. (M.D.),
         Treatment of displaced subcapital and transcervical fractures
         of the femoral neck by muscle-pedicle-bone graft and internal
         fixation, J. of B. & J. Surgery, Vol. 55-A, No. 1, pp. 257-274
         (March 1973).

[45] Salvak, E. (M.D.), Long term results of femoral head replacement,
         J. of B. & J. Surgery, Vol. 55-A, No. 3, (April, 1973).