

THE UNIVERSITY OF CALGARY

THE ELECTROCHEMICAL OXIDATION AND REDUCTION OF
Ni-Co GLASSY ALLOYS IN ALKALINE SOLUTIONS

by

KE LIAN

A THESIS

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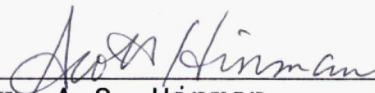
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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled, "The Electrochemical Oxidation and Reduction of Ni-Co Glassy alloys in Alkaline Solutions" submitted by Ke Lian in partial fulfillment of the requirements for the degree of Master of Science.



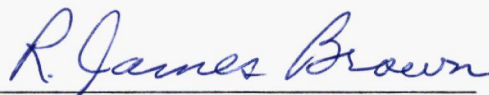
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ABSTRACT

The electrochemical oxidation and reduction behavior of a glassy alloy, having the composition of $\text{Ni}_{51}\text{Co}_{23}\text{Cr}_{10}\text{Mo}_7\text{-Fe}_{5.5}\text{B}_{3.5}$ (weight percentages), has been investigated in alkaline solutions in the present work. Cyclic voltammetry and potentiostatic methods have been utilized in the electrochemistry study, while XPS, AES and SEM have been used for the surface analyses.

It has been found that, in 1 M NaOH solutions, surface-enriched Cr (and Mo) is dissolved at positive potentials, as shown by the solution analysis and XPS/AES results. With the use of potential cycling techniques, a thick hydrous Ni/Co oxide film can be formed on the alloy surface. The oxide, which is very similar to hydrous Ir oxide films, is micro-porous, ion- and solvent-filled, and electrochromic. It oxidizes and reduces via an electron hopping process between metal sites, with the concurrent injection and expulsion of ions into/out of the film.

In comparison with the electrochemical behavior of individual Ni, Co, and co-precipitated Ni-Co alloy electrodes, hydrous Ni/Co oxides display many special characteristics, although their CV responses appear very similar to those of Ni electrodes. It has also been found that the electrochemical behavior of hydrous Ni/Co oxide films has many similarities to that of polymer modified electrodes.

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FOR MY DEAR PARENTS

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LIST OF MAJOR SYMBOLS

<u>Symbol</u>	<u>meaning</u>
A_{app}	apparent area
A_0, A_1, A_2, A_3, A_4	anodic peaks
C	concentration of electroactive species
C_1, C_1', C_2, C_3	cathodic peaks
D	diffusion coefficient
D_{app}	apparent diffusion coefficient
d	thickness of oxide film
E	electrode potential
E^0	standard potential of an electrode
$E^{0'}$	formal potential of an electrode
E_h	healing potential
E_m	potential at middle point of anodic and cathodic peaks
E_p	pitting potential
$E(+)$	positive limit of potential scan or pulse
$E(-)$	negative limit of potential scan or pulse
$\Delta E_{1/2}$	peak-width-at-half-height in CV
F	Faraday's constant, 96487 C/equiv.
g	interaction parameter

I	current
I_{cp}	cathodic current
i	current density
k	rate constant
M	1) metals (Ni and Co) 2) mol/l
n	1) number of electron involved in a reaction 2) number of layers of film
N	normality
Q	charge passed during a reaction
Q_a	charge passed in anodic reaction
Q_c	charge passed in cathodic reaction
Q_i	cathodic charge obtained in CV from the second potential scan)
Q_t	cathodic charge in CV at time t
q	charge density
q_a	anodic charge density
q_c	cathodic charge density
q_i	initial charge density obtained from the second potential scan)
R	gas constant
s	potential sweep rate
s_c	cathodic potential sweep rate
T	absolute temperature
t	time

V

volume of oxide film

LIST OF MAJOR ABBREVIATIONS

<u>Abbreviation</u>	<u>Meaning</u>
AAS	Atomic Absorption Spectroscopy
AES	Auger Electron Spectroscopy
cd	current density
CE	counter electrode
CV	cyclic voltammetry, or, cyclic voltammogram
HCL	hollow cathode lamp
HER	hydrogen evolution reaction
OCP	open circuit potential
OER	oxygen evolution reaction
rds	rate determining step
RE	reference electrode
RHE	reversible hydrogen electrode
SAM	Scanning Auger Microprobe
SCE	saturated calomel electrode
SEM	Scanning Electron Microscopy
SHE	standard hydrogen electrode
WE	working electrode
XPS	X-ray Photoelectron Spectroscopy

Chapter 1

INTRODUCTION

1.1 Introduction

Glassy alloys, also called metallic glasses, are relatively new materials which are primarily metallic in composition, but have an essentially noncrystalline structure, with only some short-range atomic order [1,2]. Many of these alloys possess unique mechanical, electrical, chemical and soft-magnetic properties, which are superior to those of conventional crystalline materials [1-7].

Glassy alloys are produced by a variety of techniques including melt-spinning, electrodeposition, sputtering, ion plating, etc. [1,2,8]. Among these methods, melt-spinning is the most common. In this method, a jet of molten metal is driven onto the surface of a rotating metal disk or cylinder at or below room temperature, and is solidified in the form of very thin ribbon at an extremely high cooling rate (10^6 °C/s). The first paper reporting that a glassy alloy (Au-Si) could be prepared by this method appeared in 1960 [9]. Since then, a significant amount of research has been carried out with glassy alloys, both for fundamental and technological reasons [3,10].

The chemical and electrochemical properties of glassy alloys have been under study since the first paper was

published in 1974 [11]. Most of the research in this area has focused on the corrosion and catalytic behavior of these alloys. It has been recognized that most glassy alloys exhibit a very high corrosion resistance and that some of them also possess high electrocatalytic activity, because of their unusual amorphous structure and chemical composition [5,6,12-15,18].

1.2 Purpose of Research

In the last few years, most of the studies dealing with the electrochemical properties of glassy alloys have concentrated on their corrosion behavior in acidic media [7,12-14,18]. Relatively little research has been done in alkaline media [16,17], although it is important to obtain this sort of knowledge for future practical applications of glassy alloys.

In this work, the electrochemical behavior and properties of a Ni-based glassy alloy have been investigated in aqueous alkaline solutions. The principal objectives of this work have been to understand the fundamental electrochemical behavior of this glassy alloy in comparison with that of the individual polycrystalline metals, and to deduce the mechanism of oxide film formation at this alloy. In particular, as pure Ni and Co metals have substantially different modes of oxidation from each other, it is of interest to investigate whether this Ni-based glassy alloy

containing these two elements would show characteristics which reflect the presence of both metals or whether a new type of behavior would be seen. It is also of interest to compare the electrochemical behavior of a Ni-based glassy alloy to that of a Co-based glassy alloy in order to determine their common properties. Also, the corrosion resistance of an electrochemically oxidized Ni-based glassy alloy has been tested in comparison to that of the as-quenched material.

Chapter 2

BACKGROUND OF THIS RESEARCH

2.1 Electrochemical Properties of Glassy Alloys

In 1974, Naka, Hashimoto and Masumoto [11] first reported the high corrosion resistance of some Fe-based glassy alloys, particularly in acid solutions containing chloride ions. Glassy alloys have been of interest as corrosion-resistant materials since that time.

According to Hashimoto et al., glassy alloys can be considered to be physically and chemically homogeneous. They do not contain crystalline defects such as grain boundaries, dislocation faults and segregates, which are inherent in conventional crystalline alloys and often cause their local corrosion susceptibility. Moreover, the single-phase nature of glassy alloys prevents interphase galvanic effects [15].

Glassy alloys have been divided into two compositional classes: metal-metal binary systems, and transition metal-metalloid solid solution. In the former group, binary metal-metal glasses such as Cu-Zr, Ni-Nb and Cu-Ti usually have a ca. 1:1 composition. The latter group includes Fe, Co and Ni based systems, often alloyed with other metals and combined with certain quantities (ca. 20%) of metalloidal elements such as P, B, Si and C. Most conventional crystalline alloys contain less than ca. ten percent of the metalloid

components. The chemical properties, especially the corrosion behavior, of these two classes of glassy alloys have been found to be intrinsically distinct [15,18].

Some researchers have reported the electrochemical behavior of metal-metal type glassy alloys. Grant and Archer investigated the electrochemical behavior of a binary glassy $\text{Ni}_{60}\text{Nb}_{40}$ alloy in aqueous media at different temperatures and found that this alloy possesses a combination of the properties of Ni and Nb which results in a particularly high corrosion resistance in various acidic and basic solutions [19,20]. The results obtained by Naka et al. on Cu-Zr and Cu-Ti [21] and by Turn et al. on Cu-Zr alloys [22] also support the idea that, in metal-metal glassy alloy systems, the composition of the alloy (i.e. the presence of passivating elements) plays a major role in their corrosion resistance while the structure is not such an important factor. Overall, relatively few studies have been performed on the metal-metal binary type of glassy alloy.

In contrast, the electrochemical behavior, particularly in terms of corrosion resistance, of metal-metalloid glassy alloys has been widely studied. First, it has been found that the addition of passivating elements such as Cr, Mo, Ti and Zr to these glassy alloys can dramatically increase their corrosion resistance. Of these film-forming elements, Cr has been found to be the most effective. In Cr-containing glassy alloys, a chromium-enriched passive film is formed on the

surface of the alloy. This film is composed mainly of hydrated chromium oxy-hydroxide, $\text{CrO}_x(\text{OH})_{3-2x} \cdot n\text{H}_2\text{O}$ ($x = 0$ or 1) [23,24], which is very protective in chloride-containing acidic and neutral solutions. This passive film is also thought to form on crystalline stainless steels [12], but the amount of Cr needed to have the same protective effect is much greater than that in the glassy alloy. Cr enrichment is considered to occur by the rapid selective dissolution of alloy constituents which are unnecessary for passive film formation, if the alloy is in acidic solution [12-18]. It also occurs even in the air-formed film on both glassy alloys and conventional Fe-Cr alloys [24,25].

Second, it has been recognized that the addition of large amounts of metalloids (ca. 20%) significantly affects the chemical properties of metal-metalloid glassy alloys. Large quantities of metalloids cannot be added to crystalline alloys, since they can become brittle, and chemically unstable multiphases may form [12]. The metalloid addition may result in a decrease of the corrosion current density at the corrosion potential because of the low exchange current density of the hydrogen evolution reaction (HER) at metalloids.

Metalloids, such as phosphorus, have been found to affect passive film formation as well [12-15,26]. Hashimoto and co-workers reported a synergistic effect between chromium and phosphorus in glassy alloys [12]. The results obtained by

Diegle and other researchers [18] showed that P is enriched in the inner oxide while Cr^{+3} is enriched in the outer oxide region, and P may serve as a diffusion barrier to aggressive ions such as Cl^- , etc [18]. Research has also been carried out on other metalloid elements such as C, B and Si. It was found that boron and silicon often constitute the surface region as chromium borate or silicate, which somewhat reduces the concentration of Cr in the passive film [7]. Although the real cause of Cr-P synergism is still unclear, one can conclude from the literature that phosphorus is the most effective metalloid element for improving the corrosion resistance of Cr-containing transition metal-metalloid glassy alloys.

The electrocatalytic properties of glassy alloys have also been investigated by numerous researchers. There is evidence that some of the glassy alloys exhibit greater activity and longer catalyst life than their crystalline counterparts, although the cause of this is not clear. Glassy alloys which have been reported to exhibit a high catalytic activity towards various electron transfer reactions are Cu-Ti [27] and $\text{Fe}_{60}\text{Co}_{20}\text{Si}_{10}\text{B}_{10}$ [28] alloys for the hydrogen evolution reaction (HER), $\text{Co}_{50}\text{Ni}_{25}\text{Si}_{15}\text{B}_{10}$ [28] for the oxygen evolution reaction (OER), $\text{Pd}_{35}\text{Zr}_{65}$ and $\text{Ni}_{63}\text{Zr}_{37}$ for hydrogenation of carbon monoxide [29] and some Pd-Ir glassy alloys for chlorine evolution [30]. However, some glassy alloys possess rather unfavorable characteristics

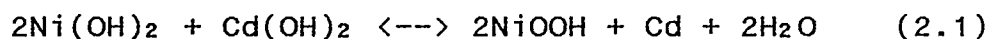
in terms of electrocatalysis and have a lower catalytic activity than their crystalline counterparts [31,32].

2.2 Electrochemical Behavior of Ni, Co and Related Metals and Alloys

Since the glassy alloy being studied in this work is composed mainly of nickel, cobalt, chromium and molybdenum, it is necessary to review the relevant electrochemistry of these metals.

2.2.1 Nickel, Nickel Oxides and Their Electrochemistry

There has been great interest in Ni oxides as battery materials since the beginning of this century, when the Ni-Fe battery was invented by Edison [33] and the Ni-Cd battery by Junger [34]. The latter is still widely used at the present time, especially for airplanes. In Ni-Cd batteries, Ni oxide and Cd metal are used as the positive and negative electrodes, respectively. During the charging process, the active material of the positive plate is oxidized from Ni(OH)_2 to NiOOH , while the Cd hydroxide at the negative plate is reduced to metal [35,36], according to the following reaction,



and vice versa in the discharging process.

Ni oxides can be formed both chemically and electrochemically. In the former case, NiO can be obtained by

heating Ni metal [37,38], and higher oxides than NiO such as Ni₂O₃ and NiO₂ may be obtained by carefully heating Ni(NO₃)₂ or Ni(OH)₂ under controlled conditions [39-41]. The structure of these thermally prepared Ni oxides has been determined by x-ray diffraction studies and has been found to be face-centered cubic [42,43].

The electrochemical formation and properties of Ni oxides and hydroxides in aqueous solutions have been studied for years. Some primary conclusions have been made, although there are still some controversial issues remaining. In acid solutions, Ni might be passivated at low potential but will dissolve as Ni⁺² ions [44,45] at higher potential. In neutral and basic solutions, Ni is passivated by a stable oxide film, which has been given particular attention in the studies of Ni electrodes.

Generally, Ni electrodes undergo a series of reactions including the hydrogen evolution reaction (HER), Ni/Ni(OH)₂, Ni(OH)₂/NiOOH transformations and the oxygen evolution reaction (OER), from negative to positive potentials in alkaline solutions [46-51]. The structures of Ni(OH)₂ and NiOOH were analysed by Bode and co-workers [51] by x-ray diffraction. It has been found that both of these oxides exist in two forms, α and β for Ni(OH)₂, β and γ for NiOOH, where α -Ni(OH)₂ is oxidized to γ -NiOOH and β -Ni(OH)₂ to β -NiOOH, respectively. The reactions could be shown as a Bode's diagram [51]:



Although the presence of Ni(IV) species (e.g. NiO₂) is possible, NiOOH is considered as the highest oxidation state of Ni since NiO₂ is so unstable that it decomposes rapidly [44,52,53].

Numerous researchers have investigated the mechanism of Ni oxide formation from various avenues. In the early studies, the oxidation/reduction of Ni oxides and hydroxides was considered to take place in the solid-state. Briggs et al [54,55] used potentiostatic methods to study the oxidation of solid $\alpha\text{-Ni(OH)}_2$ in KOH solution. The anodic process (i.e. Ni(OH)₂ to NiOOH), they believed, was controlled by nucleation, growth and overlap of NiOOH nuclei, which is similar to the cases of Pb and Ag oxides. The cathodic process was controlled either by proton diffusion within the lattices of the oxide or by cation transfer with a diffusion coefficient (D) of about $10^{-10} \text{ cm}^2\text{s}^{-1}$.

The D of the cathodic process is similar to the data obtained by MacArthur [56]. In his paper, it was assumed that the rate of the oxidation reaction was controlled by proton diffusion in the solid-state towards the electrolyte, reacting with OH⁻ to form H₂O, and reduction was controlled by proton diffusion towards the lattice to fill the proton vacancy. Other authors, such as Weininger and Breiter [49,50], Arvia et al. [48,57,58], Hahn et al. [59,60],

Visscher et al. [61], Park et al. [62], etc. have studied Ni electrodes extensively as well.

Although many authors have been aware of the participation of H_2O and ion-exchange processes in the oxidation and reduction of Ni hydroxide [56,63-65], the interpretations are neither clear nor unified but somewhat overlapped. No real progress was made until recently, when the concept of "hydrous oxides" was introduced by Burke et al. [46,47,66-68]. Hydrous oxides, often formed electrochemically at polycrystalline metals such as Ir [66,69], Rh [67], W [70], Co [71] etc., have been found to possess some special properties which are of considerable interest in their application in batteries, electrochromic devices and electrocatalysis. The special characteristics of hydrous oxides could be attributed to their unusual microstructure and their electrochemistry.

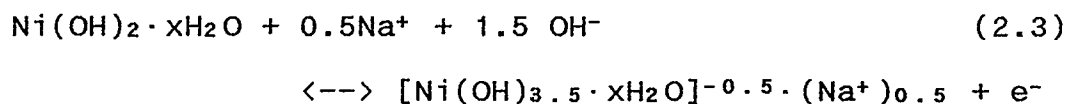
Micromorphologically, hydrous oxides appear to have a solvent-filled, highly microporous polymeric structure, in which metal ion sites are linked by partially covalent oxygen (M-O-M) and hydroxy (M-O--H--O-M) bridges [68,72,73 102]. Electrochemically, hydrous oxides exhibit a special potential-pH dependence of ca. 70 to 90 mV per pH unit with respect to a pH-independent reference electrode [74,75], unlike those of conventional oxide electrodes which usually show 60 mV/pH unit potential-pH relationships [44,76]. During the oxidation and reduction of these oxides, the metal

ion sites in the hydrous oxide, which are not readily reduced to metal, oxidize and reduce via a site-to-site electron hopping mechanism, while counterions from the electrolyte are injected/ejected from the oxide film in order to maintain electroneutrality [73,74,77, 102]. Furthermore, most of the hydrous oxides show electrochromic behavior [47,66,67,70].

Burke et al. investigated polycrystalline Ni electrodes in alkaline solutions from the 'hydrous oxide' point of view [46,47,75]. They reported that a thick hydrous oxide film can be formed on the Ni electrode by a potential cycling technique. According to Burke [46], Ni hydrous oxide consists of two kinds of oxide, the inner, anhydrous (β -Ni(OH)₂ and β -NiOOH), and outer, hydrous (α -Ni(OH)₂, γ -NiOOH·H₂O) oxides, respectively. Two pairs of peaks are expected for Ni(II)/Ni(III) oxide transformation. The first pair of peaks, corresponding to β -Ni(OH)₂ and β -NiOOH conversion, has a normal 60 mV/pH dependence.



This is in agreement with the reaction suggested by Bode and other authors [51,59]. However, the second pair of peaks, corresponding to α/γ hydrous oxides transition, shows an unusual pH-potential relationship (i.e. 88.6 mV/pH unit versus pH-independent reference electrode). The reaction can be written as follows:



and vice versa in the reduction process. In the hydrous oxide layers, the planar metal hydroxide layers have been separated from one another by planes of water molecules and electrolyte (in γ -NiOOH) [46]. Also, Burke suggests several reaction schemes which are different from Bode and other authors [51,59] (to be discussed in section 4.1). Although the mechanism of oxide formation at Ni electrodes is still not very clear, the 'hydrous oxide' does provide a promising approach to understand the oxidation and reduction processes on Ni and other similar transition metals.

2.2.2 Cobalt, Ni-Co Alloys and Their Electrochemistry

Compared with Ni, the electrochemical behavior of Co is more complex but has been less studied. Recently, several papers have appeared in the literature, primarily in relation to the electrocatalytic properties of Co oxides and hydroxides. In particular, many authors have reported that cobalt can be used as an additive to nickel battery electrodes to improve their efficiency and cycle life [80-82].

As with Ni hydroxide, there are also views in terms of the interpretation of the nature and the structure of electrochemically formed Co oxides. The solid-state approach indicates that cobalt hydroxide consists of α - and β -Co(OH)₂ phases, and β - and γ -CoOOH phases, which are comparable to oxides formed at Ni electrodes [51].

Researchers have used various electrochemical methods to investigate Co oxides, and have suggested the formation of Co(OH)_2 via a solid phase mechanism [83,84]. Arvia et al. reported that the Co oxide/hydroxide electrode may have a sandwich-type of structure, i.e. cobalt electrode/inner film/outer film/solution interface [85,86]. Furthermore, the electrochemical reactions are thought to involve fast proton transfer and further oxidation of the electrode may be accompanied by deprotonation and a change of the water content in the oxide at different parts of the complex interfaces [86].

Burke et al. [71,78] have again considered electrochemically formed Co oxides as hydrous oxides. They reported that the general pattern of oxide growth and the electrochromic behavior of cobalt oxide electrodes under potential cycling conditions are quite similar to those of other metals which form hydrous oxides, including Ni, Ir, Au etc [71,78].

Ni-Co crystalline alloys have also been examined, both in terms of their thermal and electrochemical oxidation. From the solid-state viewpoint, Wood et al. [87] studied Ni-Co oxides which were thermally formed at 600 °C at 1 atm oxygen. It has been found that the oxidation of Ni-Co resulted in a solid solution of NiO and CoO, in which CoO formed towards the outside of the oxide and NiO more towards the alloy/oxide interface. This has been attributed to the fact that Co^{2+} diffuses faster than Ni^{2+} . The oxidation rate of the Ni-Co

alloy was found to be faster than that of pure Ni. This is due principally to the increase of vacancies in the oxide. Similar results were also obtained by Majumdar et al. from XPS and AES studies [88].

Pickett and Malay [82] investigated electrochemically co-precipitated Co hydroxide/Ni hydroxide electrodes by microelectrode techniques. It was shown that the addition of Co hydroxide improved the reversibility of the Ni hydroxide electrochemistry, with the oxidation of Ni occurring at less positive potentials than with Ni only, and the charging process occurred at a higher rate. Therefore, the co-precipitated Co(OH)_2 could be considered as an electrocatalytic agent, although the mechanism of this catalysis is not yet understood.

Haenen and Visscher [89] have also studied the electrochemical formation of oxides at Ni-Co alloys in alkaline solutions by cyclic voltammetry and ellipsometry. It is of interest that, under potential cycling conditions, the voltammetric behavior of both Ni_1Co_1 and Ni_1Co_2 are very similar to that of a pure Ni electrode. Also, the Tafel slope of Ni-Co alloy towards OER was ca. 40 mV/decade current density (cd) similar to that obtained on Ni or NiCo_2O_4 spinel-type oxides. However, if subjected to preanodization at high potentials (OER region), the electrode demonstrates a Tafel slope of 60 mV/decade cd, which was also obtained on Co or Co_3O_4 spinel-type oxides. These results have been

interpreted by postulating that, depending on the pre-treatment, different oxides or spinel-like oxides are formed on the alloy electrode.

2.2.3 Electrochemical Behavior of Chromium and Molybdenum in Alkaline Solutions

The importance of Cr as a passivating element has been discussed earlier. However, according to Pourbaix et al. [90], Cr dissolves as chromate ions CrO_4^{2-} in pH 14 solutions, if subjected to positive potentials, although very few papers have appeared in the literature dealing with this issue. Molybdenum is also considered as an important alloying element to improve the corrosion resistance of many alloys, especially in terms of chloride-ion-induced pitting. However, relatively little about the electrochemical behavior of molybdenum in alkaline solutions has been reported. According to Pourbaix [91], Mo may dissolve as molybdate (MoO_4^{2-}) in alkaline solutions. In a preliminary note [92], Hull described the cyclic voltammetric behavior of a Mo electrode, which shows that the Mo electrode undergoes dissolution in 0.1–10 M OH^- at potentials more positive than ca. 0.4 V.

Chapter 3

EXPERIMENTAL METHODS

3.1 Electrochemical Experiments

Cyclic voltammetry (CV), potential step methods (chronoamperometry, double potential step chronoamperometry, chronocoulometry), and a combination of these techniques were used in the electrochemical studies in this work. Experiments were carried out in aqueous alkaline solutions with the use of standard three-electrode circuitry.

3.1.1 Instruments

Most of the electrochemical studies were performed with a Hokuto-Denko HA301 potentiostat and a Tacussel GSATP multisegment function generator. There were also some experiments carried out with an EG&G PARC 173 Potentiostat and a PARC 175 Universal Programmer, in which the cell IR drop between working electrode (WE) and reference electrode (RE) could be compensated by a positive feedback loop.

Either an HP 7045B X/Y recorder or a Nicolet 3091 digital oscilloscope was used to record the current vs. voltage (I/E) and current vs. time (I/t) responses. The latter was used at high sweep rates, s , (dE/dt over ca. 500 mV/s) and other fast response experiments. In these experiments, data was stored in the oscilloscope and was then transferred to the X/Y

recorder.

All graphical areas were integrated by using a Houston Instruments Digitizer interfaced to an IBM personal computer to estimate the charge passed in each experiment.

Table 3-1 gives a list of the equipment used for the electrochemical experiments in this study.

3.1.2 Working Electrodes

The working electrodes employed in this work were a Ni-based glassy alloy (Alloy 1), a Co-based glassy alloy (Alloy 2), and some polycrystalline metals, such as Ni, Co, Mo and Cr. These electrodes are described as follows:

Ni-based glassy alloy: This glassy alloy, having a composition of $\text{Ni}_{51}\text{Co}_{23}\text{Cr}_{10}\text{Mo}_7\text{Fe}_{5.5}\text{B}_{3.5}$, has been studied in this work. The glassy alloy was in the form of a ribbon, 25 mm wide and 10 μm thick. The alloy appeared to have two different surfaces, one shiny and one dull, a result of the melt-spinning manufacturing process. The shiny side corresponds to contact with the inert gas medium, while the dull side is the result of contact with the roller during the rolling process. Before use, the WE was rinsed with distilled water and then cleaned ultrasonically in acetone. The apparent geometrical area, typically ca. 0.1-1.0 cm^2 , was used as the electrode surface area in all of this work, although a roughness factor (i.e. real area / apparent area) of 1.5 to 2 or more is likely. The WE was electrically

TABLE 3-1

MAKE AND MODEL OF ELECTROCHEMICAL EQUIPMENT USED

<u>INSTRUMENT</u>	<u>MANUFACTURER</u>	<u>MODEL</u>
Potentiostat	Hokuto Denko	HA-301
	EG&G Princeton Applied Research	173
Function Generator	TACUSSEL Electronique	GSATP
	EG&G Princeton Applied Research	175
Digital Multimeter	RACAL-DANA	4002
X-Y Recorder	Hewlett Packard	7045B
Oscilloscope	Nicolet	3091

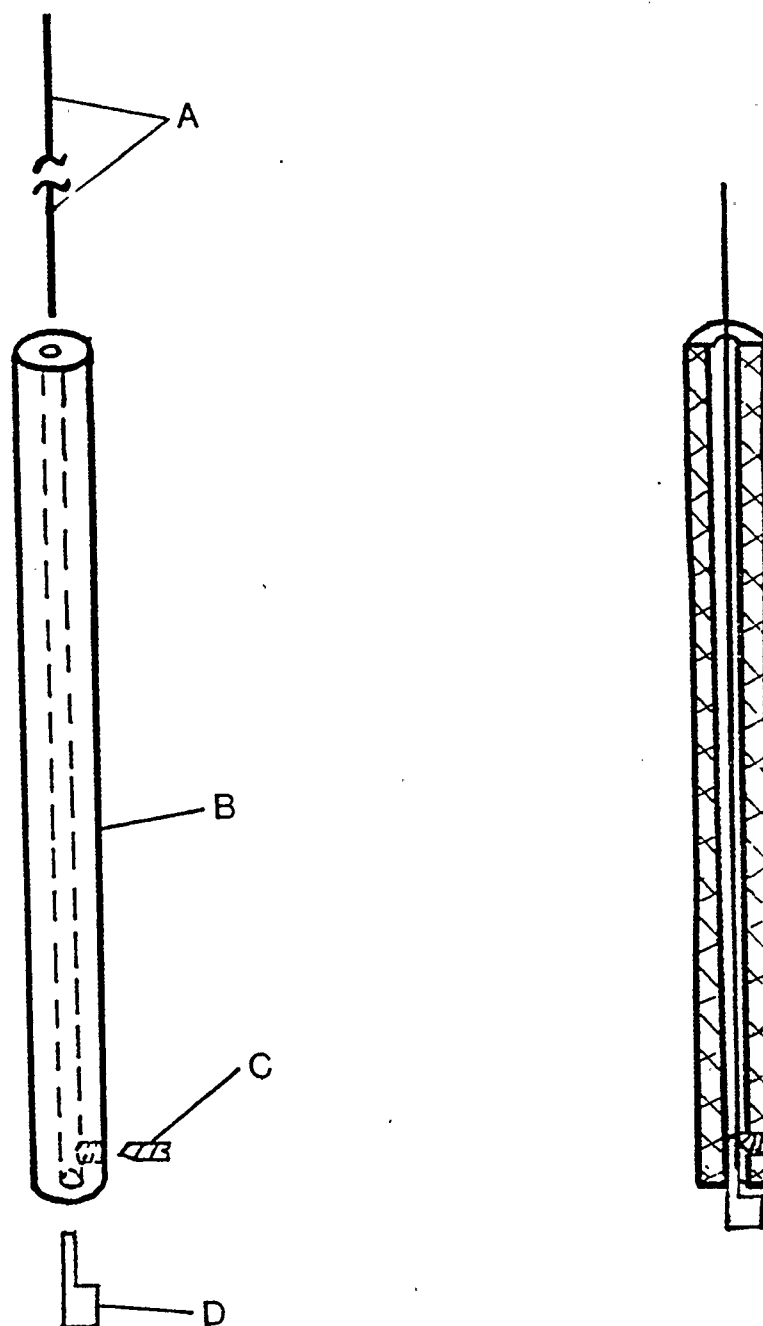


Fig. 3.1 a) Exploded view of a typical working electrode. A - silver wire, B - teflon holder, C - nylon screw, D - electrode. b) Cross sectional view of the working electrode.

connected to a silver wire, supported by a teflon holder (Fig. 3.1). Parafilm was used to cover the silver/WE junction and to enable a constant WE surface area to be studied.

In order to reuse electrodes, they were "chemically polished" between experiments by dipping the used electrodes into a 3 M H_2SO_4 solution to remove the electrochemically formed oxide film, because the alloy was too fragile to polish mechanically.

Co-based glassy alloy: The composition of this glassy alloy is $\text{Co}_{63}\text{Cr}_{27}\text{Ni}_3\text{Fe}_3\text{W}_4$. The appearance of this alloy is very similar to that of the Ni-based glassy alloy except that it is smoother, shinier and thicker (ca. 40 μm). The pretreatment of this alloy was the same as that for the Ni-based alloy.

Polycrystalline Ni, Co and Mo: The electrochemical behavior of high purity polycrystalline Ni, Co and Mo was briefly investigated in order to understand the electrochemical characteristics of the glassy alloys. These metals were used in the shape of a foil, and could be polished mechanically. Their pretreatment was the same as described for the Ni-based glassy alloy electrode.

Co-precipitated Ni/Co electrode: The electrode was made by electrodeposition of Ni and Co on a Ni substrate. The solution used was ca. 2:1 NiSO_4 and CoSO_4 with a pH about 12. The electrodeposition was performed at a constant potential

of -2.0 V (vs SCE) for about 40 to 60 seconds.

Polycrystalline Cr: Since chromium metal was not available as a plate or wire, a cube (ca. 1 cm³) of Cr was used in this study. The WE was prepared as shown in Fig. 3.2. The Cr cube was soldered to a silver wire, the solder was covered by epoxy, and then a glass tube was glued to the epoxy resin. The sides of the Cr cube were covered by parafilm. The pretreatment of this electrode was the same as that for the other WEs.

3.1.3 Reference Electrodes and Counter Electrode

The reference electrodes (RE) used in this work were either a reversible hydrogen electrode (RHE) or a saturated calomel electrode (SCE). The former was used in strong alkaline solutions and the latter in near-neutral solutions. The RHE was connected to the WE compartment by a luggin capillary. The counter electrode (CE) used in this work was a high-surface-area platinum gauze.

3.1.4 Cells and Solutions

Either a one or two compartment cell was used in this work. Figure 3.3 shows the cell arrangement used in this study. The cell had two compartments which were connected by a loosely fitting stopcock in either the open (one compartment) or closed (two compartment) position.

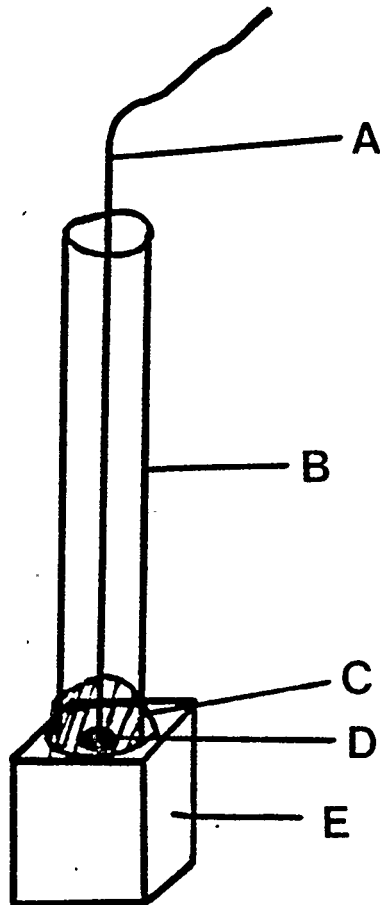


Fig. 3.2

Cr electrode. A - silver wire, B - glass tube,
C - epoxy, D - solder, E - Cr cube.

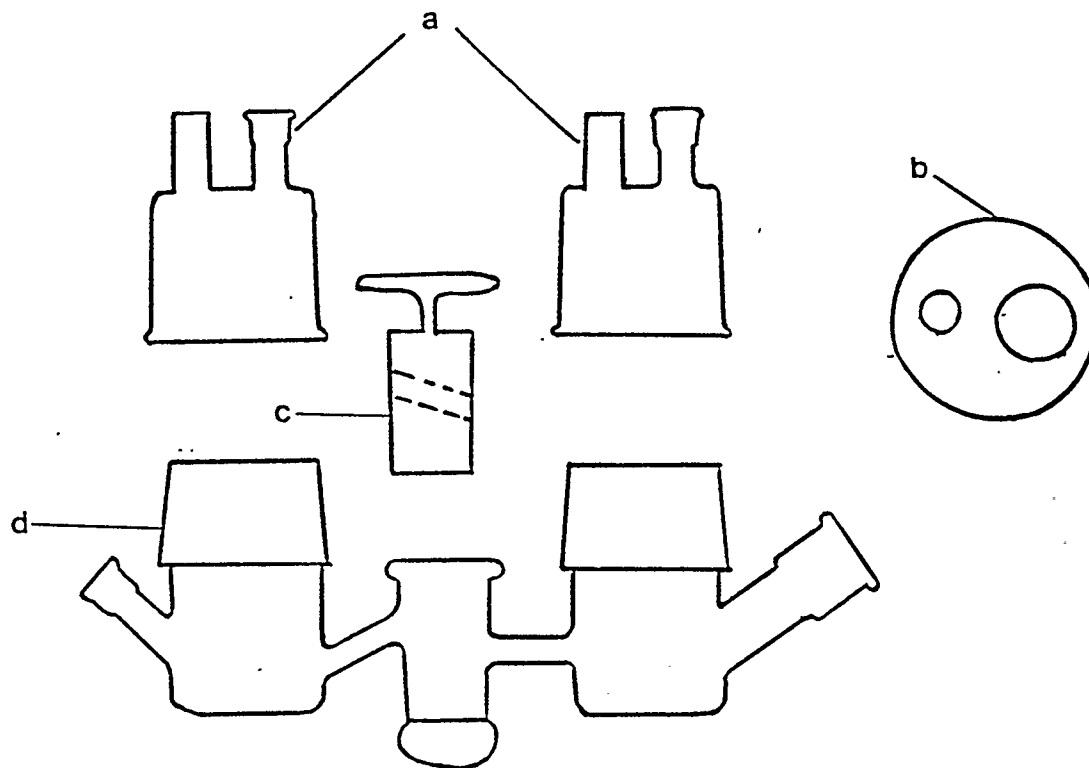


Fig. 3.3 The cyclic voltammetry and potentiostatic cell.
a - cell top. b - top view of cell top.
c - stopcock. d - cell

All of the experiments were performed in alkaline solutions of the following types:

Type 1 - Strong alkaline solutions (pH 12-14). 1 M NaOH solution was used in most of these experiments. In a series of experiments with different solution pH, various amounts of NaClO₄ were added in order to keep the ionic strength of the solutions constant.

Type 2 - Weak alkaline solutions. Borate-buffered solutions (pH 8.5-9.6), with or without added sodium chloride, were included in this type of solution.

All of the solutions were prepared by using A.C.S. reagent grade chemicals and triply distilled water. The solutions were deaerated by bubbling argon gas through or above the solution before and during the experiments. Some experiments, such as the open circuit potential (OCP) measurements, were also performed under atmospheric oxygen. Most of the experiments were carried out without stirring, since stirring did not affect the results. All experiments were carried out at room temperature.

3.2 Surface Analytical Methods

3.2.1 Scanning Electron Microscopy (SEM)

A Cambridge S-150 SEM incorporating an Edax 711 Energy dispersive X-ray analyzer was employed to investigate the structure and composition of the various WE surfaces.

Before analysis, the WE was washed ultrasonically in

water, and then attached to a graphite carbon stub using high purity silver paint. In order to estimate the thickness of surface films via examination of its cross section, the sample was bent at liquid nitrogen temperature. By this method, the 'mud-cracked' structure of the surface oxide was more clearly seen, and some part of the film could be removed, and examined separately.

3.2.2 X-ray Photoelectron Spectroscopy (XPS), Auger Electron Spectroscopy (AES) and Scanning Auger Microprobe (SAM)

In the present work, XPS, AES and SAM were employed for the surface analysis of the Ni-based glassy alloy. Accompanying these methods, an Ar ion beam is used to sputter the surface for depth analysis. Although the true sputtering rate is not known for this particular glassy alloy, the relative thicknesses of oxide film can be determined if identical sputtering rates are used. The experiments were performed on a PHY 548 XPS/AES, and a PHY 600 SAM at CANMET, Department of Energy, Mines and Resources, Ottawa, and on a VG ESCA III, at Alcan International Ltd., Kingston Laboratories.

The samples were washed in distilled water and acetone and then placed in vials filled with Ar gas for shipment to these laboratories.

3.3 Other Experimental Methods

An I.L. VIDEO 11 AA/AE Spectrophotometer was used for the Atomic Absorption Spectroscopic (AAS) analysis of the cell solutions for their Ni, Co, Cr etc. content. An N_2O -acetylene fuel-rich flame was utilized for the determination of Cr, and an air/acetylene fuel-lean flame for Ni and Co.

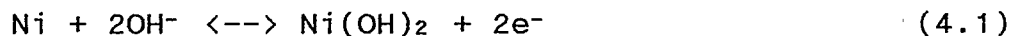
Chapter 4

ELECTROCHEMICAL BEHAVIOR OF Ni, Co, Cr AND Mo

The experiments with polycrystalline nickel, cobalt, chromium and molybdenum electrodes in alkaline solutions were initially carried out in order to compare with the electrochemical behavior of glassy alloys which are composed of these metals.

4.1 Electrochemical Behavior of Ni

A typical CV of a Ni electrode in a 1 M NaOH solution is shown in Fig. 4.1. At a sweep of 100 mV/s, two anodic peaks (A_0 and A_1) appear at ca. 0.2–0.3 V (vs RHE) and 1.4–1.45 V, respectively. No cathodic counterpart for A_0 , but one cathodic peak and one "shoulder" corresponding to A_1 , were observed. As is well known [58–62], peak A_0 is considered to be due to the transformation of Ni to Ni(OH)_2 ,



which has a standard potential (E^0) of 0.11 V (vs RHE) [44]. The absence of a cathodic peak for A_0 implies that Ni(OH)_2 is very difficult to reduce to Ni metal, even when the potential is extended into the HER region. Similar observations have also been reported by numerous previous researchers [48,53, 61]. Investigations of Ni(OH)_2 have also found that it is a poor electronic conductor but a good proton conductor

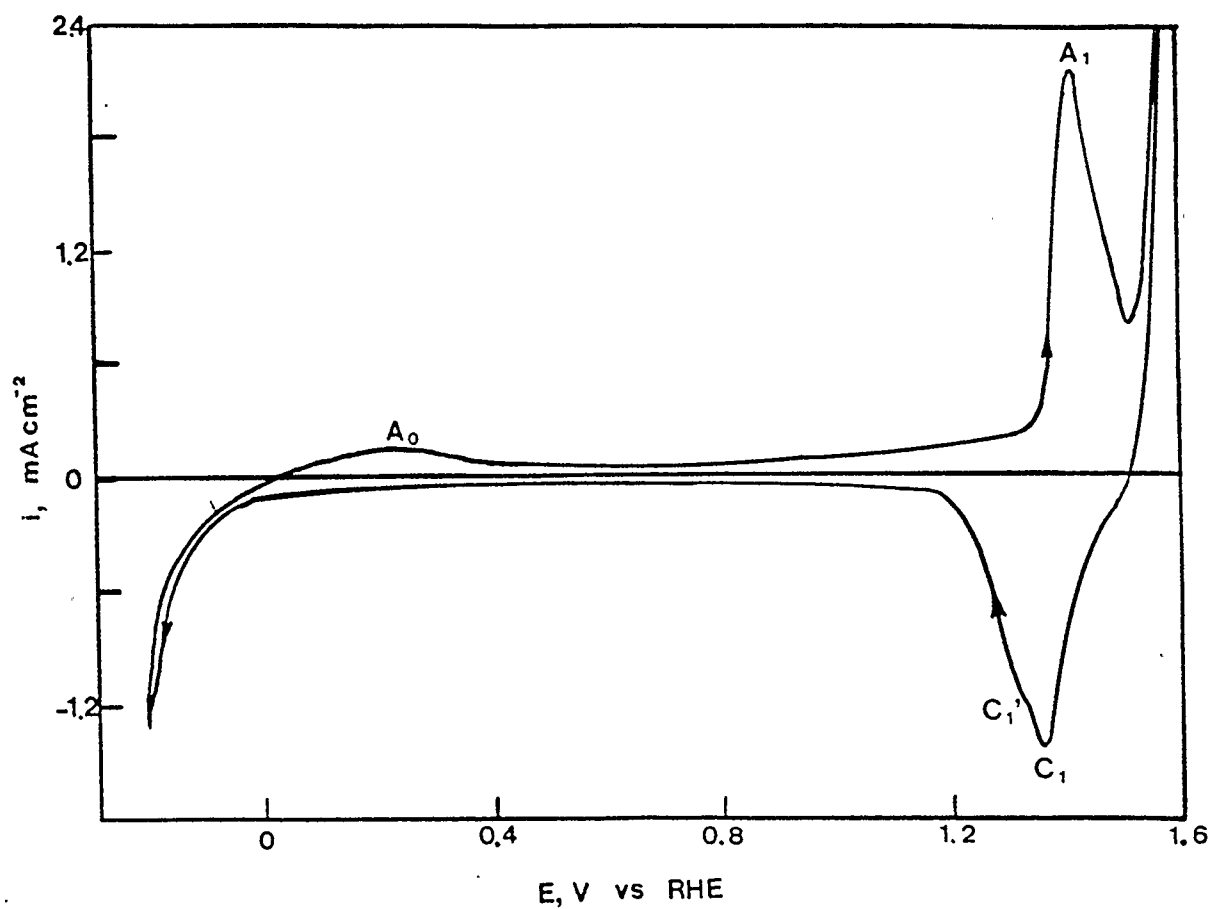
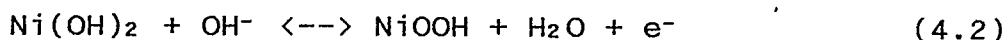


Fig. 4.1

A typical CV for polycrystalline Ni electrode
in 1 M NaOH, $s = 100 \text{ mV/s}$.

[53,65]. This poorly conducting $\text{Ni}(\text{OH})_2$ "passivates" the Ni surface until the potential is increased to a value where oxidation of $\text{Ni}(\text{OH})_2$ to NiOOH (peak A_1) takes place.



Reaction (4.2) is reflected by peaks A_1 and C_1 in the CV, with a cathodic charge density (q_c) of 3 to 5 mC/cm^2 in the first potential scan. The reported E^0 values for this reaction (4.2) have a range of values from 1.03 to 1.45 V vs. RHE [44,52]. In this work, the peak potential of A_1 varies from 1.41 to 1.47 V (vs. RHE). Peak A_1 may also overlap the OER and the formation of unstable NiO_2 , although the latter are not obvious from the CV. There are two cathodic peaks (C_1 and C_1') both corresponding to peak A_1 .

With repeated potential cycling, the currents of peaks A_1 and C_1 increase gradually. Also, the current corresponding to the HER and A_0 also increase, but at a slow rate. The latter observation may indicate that the surface is being roughened. However, the greater increase of peaks A_1 and C_1 implies the formation and growth of oxide at the Ni electrode. Similar CVs were also reported by Burke et al. [46,47].

Under the best oxide growth conditions, i.e. using a negative potential limit $E_{(-)}$ of -0.5 V and a positive potential limit $E_{(+)}$ of +1.55 V [47], the q increases at a rate of 0.37 to 0.57 mC/cm^2 per cycle (Fig. 4.2). Since the Ni electrode was mechanically polished, the roughness factor

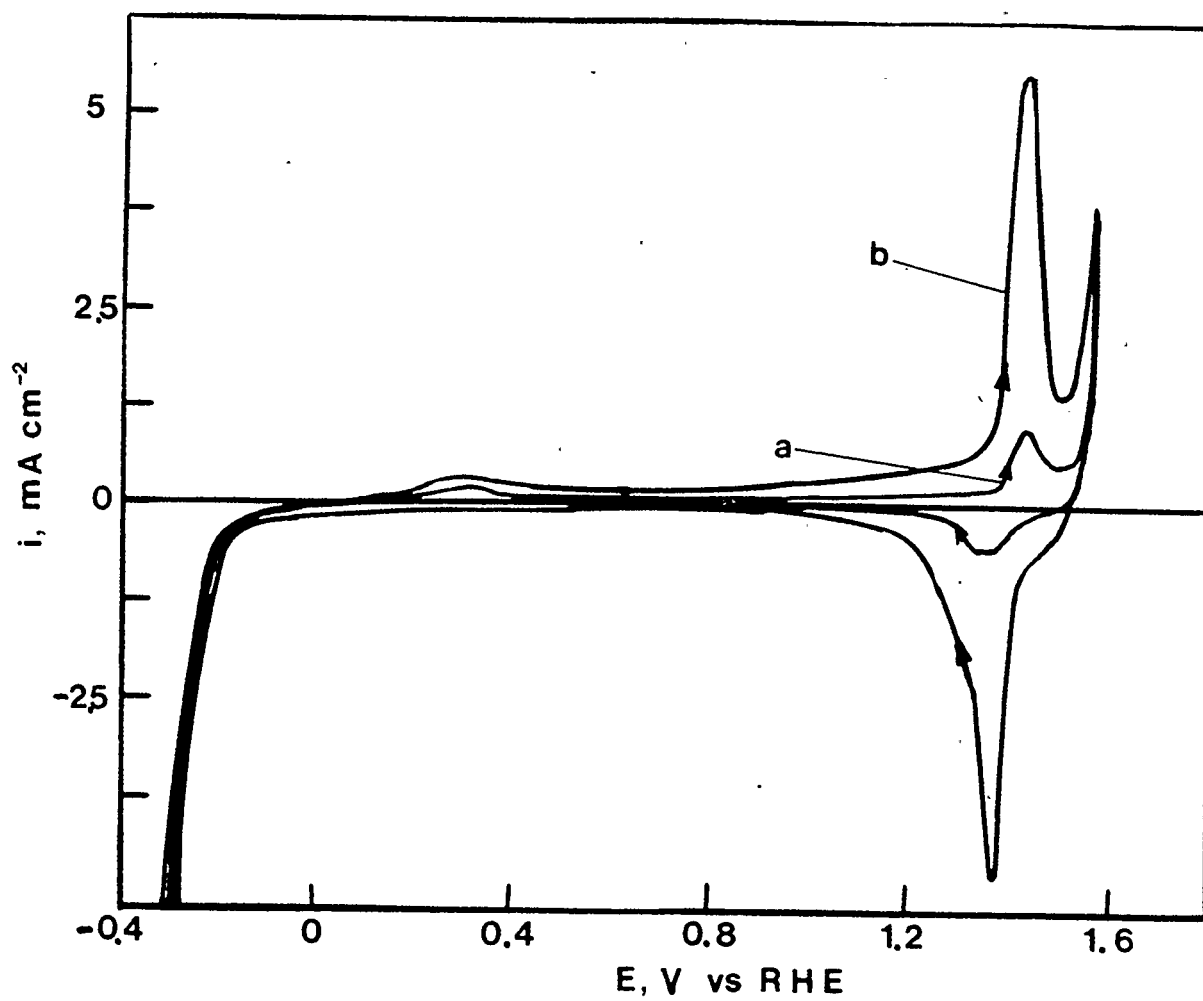


Fig. 4.2a

CVs for Ni in 1 M NaOH, $s = 30 \text{ mV/s}$; (curve a) after initial potential scan; (curve b) after 50 min. scan

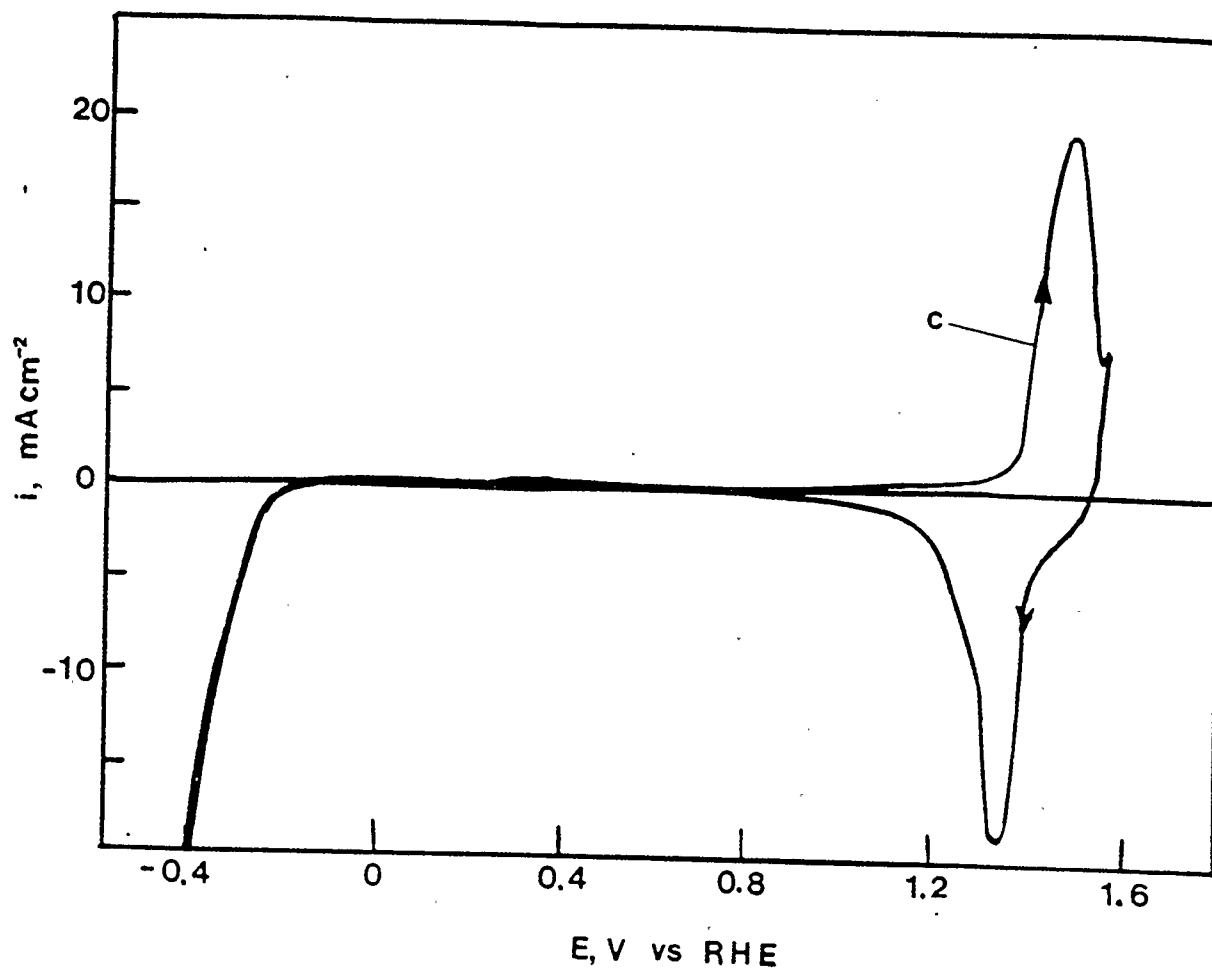


Fig. 4.2b

CV for Ni in 1 M NaOH, $s = 30 \text{ mV/s}$; (curve c) after 255 min. potential scan.

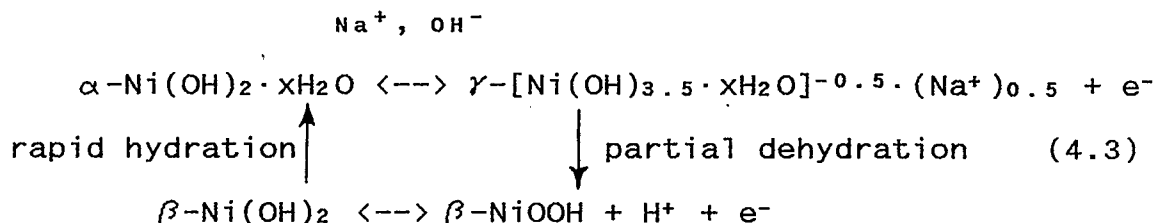
could be 2 to 3. After 50 minutes of potential cycling, the q_c of peak A_1 is about 15.7 mC/cm^2 (Fig. 4.2, curve b). After 255 minutes of cycling, the charge density has increased to ca. 77.7 mC/cm^2 (Fig. 4.2, curve c), and an electrochromic behavior, from light brown at lower potential to dark brown at more positive potentials (beyond peak A_1) was observed. The electrochromic behavior on the Ni electrode, which is typical of hydrous oxides, was also seen by Burke et al [47].

Similar CVs and general observations have also been reported by numerous authors [48,59,60,61], but the interpretations of these results have been somewhat varied. As mentioned in Chapter 2, both α - and β -Ni(OH)₂ and β - and γ -NiOOH phases have been proposed [51]. These species (e.g. α and β -Ni(OH)₂) are different, not only in their crystalline structure, but also in their electrochemical behavior.

According to Arvia et al., using potential perturbation experiments [48,57,58], Hahn et al., using in-situ UV-Vis and IR spectroscopic studies [59,60], and Visscher et al., using in-situ ellipsometric work [61], α -Ni(OH)₂ is formed by the initial oxidation of Ni metal and is then chemically converted to β -Ni(OH)₂. At higher potentials, the transformation of left-over α -Ni(OH)₂ to γ -NiOOH, and β -Ni(OH)₂ to β -NiOOH occurs (e.g. Fig 4.1), and both β - and γ -NiOOH are reduced, as summarized in Bode's diagram [51] (section 2.2.1).

According to Burke [75], based on a 'hydrous oxide'

model, two anodic and two cathodic peaks are expected for the Ni(II)/ Ni(III) transformation (see section 2.2.1). However, at a solution pH of 14, only one anodic peak having ca. 90 mV/pH dependence and two cathodic peaks, one with a ca. 90 mV/pH dependence, and one with a 60 mV/pH dependence, were obtained [75]. Burke explains the absence of one anodic peak by assuming the rapid hydration of β -Ni(OH)₂ to α -Ni(OH)₂, so that only the α -Ni(OH)₂/ γ -NiOOH transformation peak is seen. He further assumes that γ -NiOOH, which is the hydrous form of NiOOH, then partially dehydrates to β -NiOOH, so that both γ/α and β/β (Ni(III) to Ni(II)) transformation peaks are seen in two cathodic peaks. Burke's suggestion are summarized below:



where both α - and β -Ni(OH)₂ are formed electrochemically. Reaction (4.3) is different from the reaction scheme suggested by Bode (reaction 2.2).

In the present work, only one anodic peak (A₁) and two cathodic peaks (C₁ and C₁') for the Ni(OH)₂/NiOOH transformations are seen (Figs. 4.1 and 4.2), similarly to the results obtained by Burke [46,75]. No attempt was made to test the pH dependence of these peaks. However, by comparison of the potentials of these peaks with Burke's [46,75] and Arvia's [57] results, peaks A₁ and C₁ clearly

correspond to the oxidation and reduction of α/γ oxides, which should have a ca. 90 mV/pH dependence, while peak C_1' could be the reduction peak of β -NiOOH to β -Ni(OH)₂.

Although the appearance of the CVs (Figs. 4.1 and 4.2) seem in agreement with the interpretation suggested by Burke, an experiment involving gradually increasing $E_{(+)}$ values (Fig. 4.3) shows an interesting result. When the potential was scanned to a critical $E_{(+)}$ of 1.405 V, only peak C_1' was observed in the cathodic scan (Fig. 4.3, curve b). This implies that some β -Ni(OH)₂ is present in the oxide, but its oxidation may overlap with the hydrous α/γ oxide oxidation peak. Therefore, in pH 14 (or less) solutions, both α , γ (hydrous) and β , β (anhydrous, possibly crystalline) oxides may exist at the Ni electrodes under the experimental conditions, although the oxidation of α - and β -Ni(OH)₂ overlap so that only one anodic peak is seen.

The ratio of hydrous to anhydrous oxide appears to vary with experimental conditions. This is demonstrated in Fig. 4.4. When the potential was repeatedly scanned in a range in which $E_{(-)}$ was increased to ca. 0.98 V and $E_{(+)}$ was ca. 1.52 V, peak C_1 (hydrous oxide) increased and C_1' (anhydrous compact oxide) decreased, although the total charge was constant. This result implies that anhydrous β -NiOOH tends to be converted to a hydrated form if $E_{(-)}$ is maintained at positive values. Also, a relatively lower $E_{(+)}$ (less OER) may prevent the dehydration of γ -type oxide.

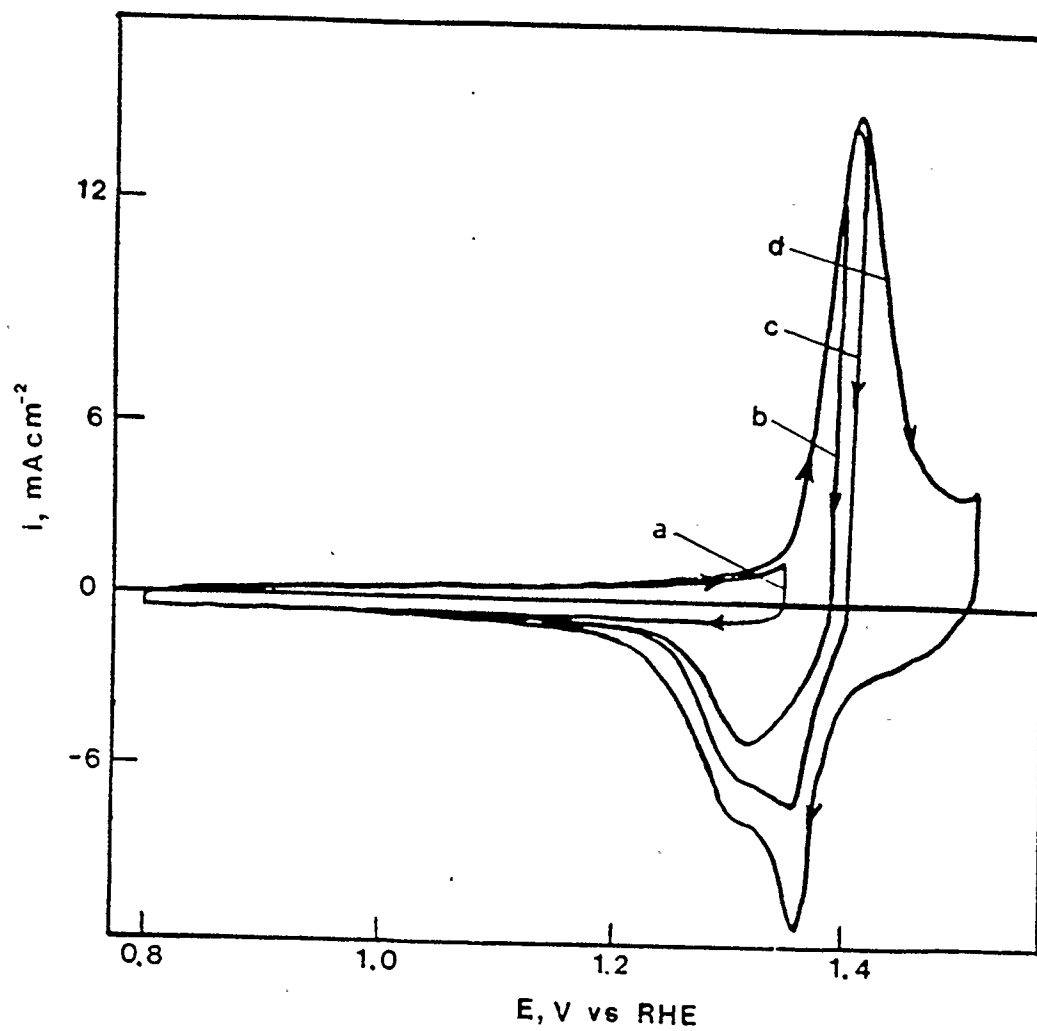


Fig. 4.3

CVs for Ni electrode with different $E(+)$, in 1 M NaOH. $s = 100 \text{ mV/s}$.

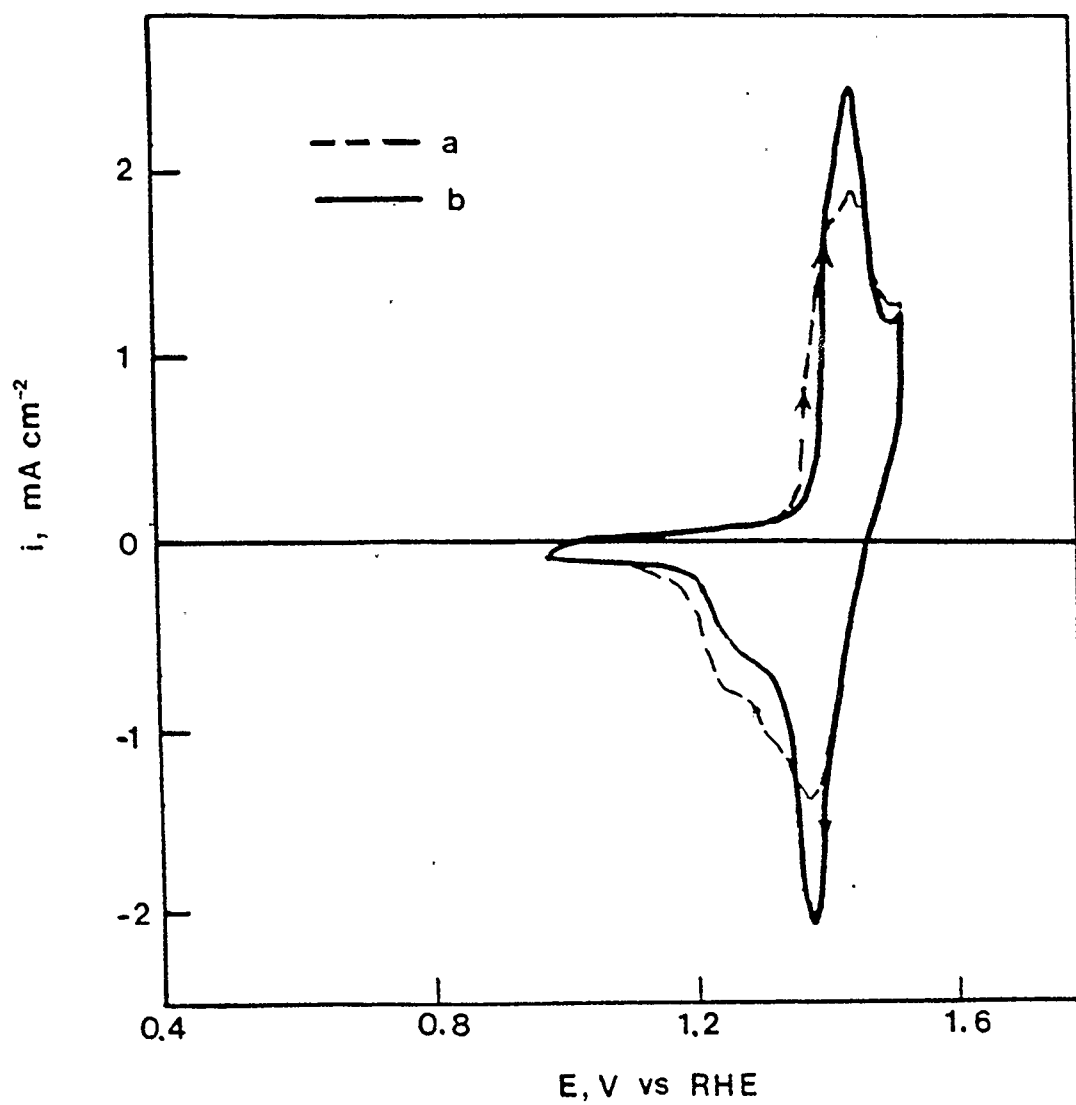
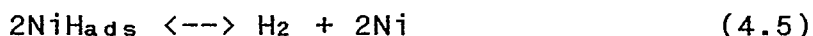


Fig. 4.4

CVs for Ni electrode in 1 M NaOH at high $E(-)$, $s = 30 \text{ mV/s}$; (curve a) 4th scan; (curve b) after 72 min. scan.

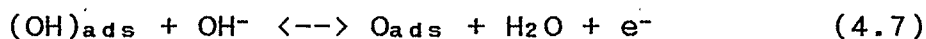
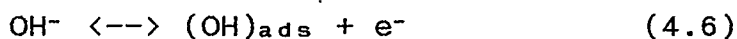
The surfaces of these electrochemically formed Ni oxides were examined by scanning electron microscopy. The scanning electron micrograph of the oxidized Ni electrode (Fig. 4.5) shows that the oxide has a roughened microstructure. This structure is quite different from those of typical hydrous oxides (e.g. on Ir) [72,102], which have smooth, 'mud-cracked' structures.

No attempt was made to determine the mechanism of the HER and OER at Ni oxide electrodes, since these have been quite well established by others [28,93,94]. The Tafel slope ($dE/d\log i$) for the HER in alkaline solutions is about 120 mV/decade cd, which suggests a possible mechanism as follows [94]:



where reaction (4.4) is a likely rate determining step (rds).

In terms of the OER, two Tafel regions have been reported, 40-50 mV/decade cd at low current densities and 120 mV/decade cd at high current densities [53,95]. In the latter, the discharge of H_2O or OH^- is believed to be the rds. At low current densities, various mechanisms have been suggested [53,95,96]. One of the possible mechanisms is:



where the second electron transfer reaction (4.7) is the rds

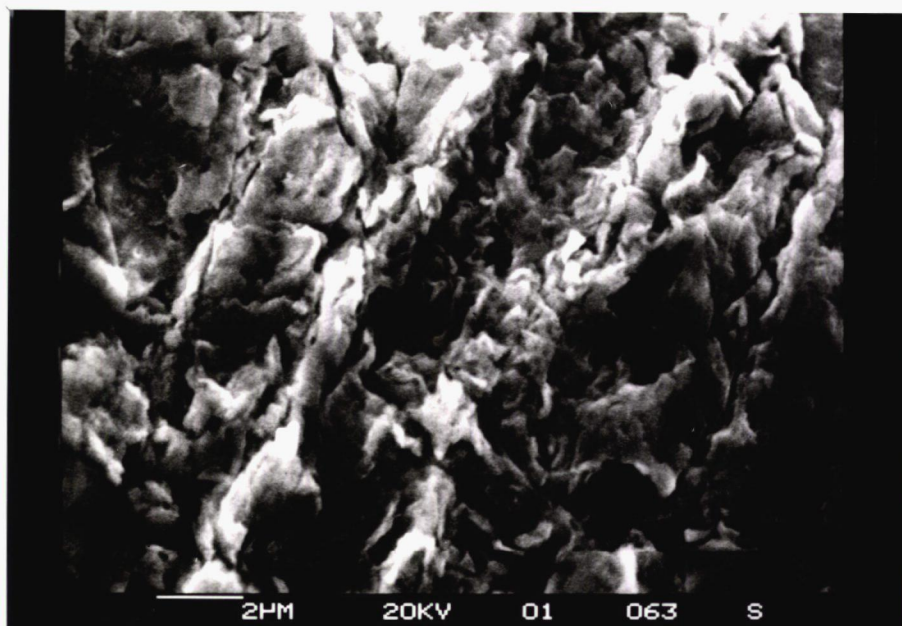
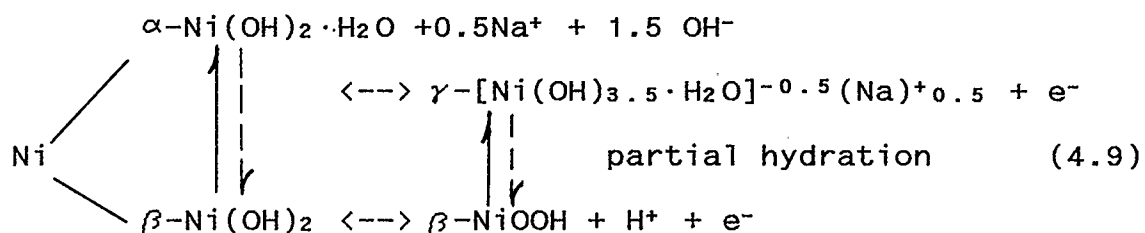


Fig. 4.5 SEM photograph of the oxide film
electrochemically formed at Ni electrode.

at low cd, and reaction (4.6) is the rds at high cd [53,96]. It has also been suggested that decomposition of NiO₂ is involved in the OER [44,53].

From the discussion above, one can conclude that the electrochemically formed Ni oxide demonstrates hydrous oxide characteristics, but has a different micromorphology than typical hydrous oxides [72,102]. The oxidation/reduction reactions of Ni/Ni oxide, under potential cycling conditions in NaOH solutions, can be summarized as follows:



where the α/γ transformation should have a ca. 90 mV/pH dependence, and Na^+ ions are involved in their oxidation and reduction in order to maintain electroneutrality of the hydrous oxide, as mentioned in Chapter 2.

4.2 Electrochemical Behavior of Co and Ni/Co Co-precipitated Alloys

The range of oxidation states and forms of stable Co oxide cause the electrochemistry of Co to be much less understood than that of Ni at the present time. However, by comparing Fig. 4.6 with the thermodynamic data calculated by Pourbaix et al. [97] and with the experimental data obtained by Behl and Toni [83], who first applied cyclic voltammetry

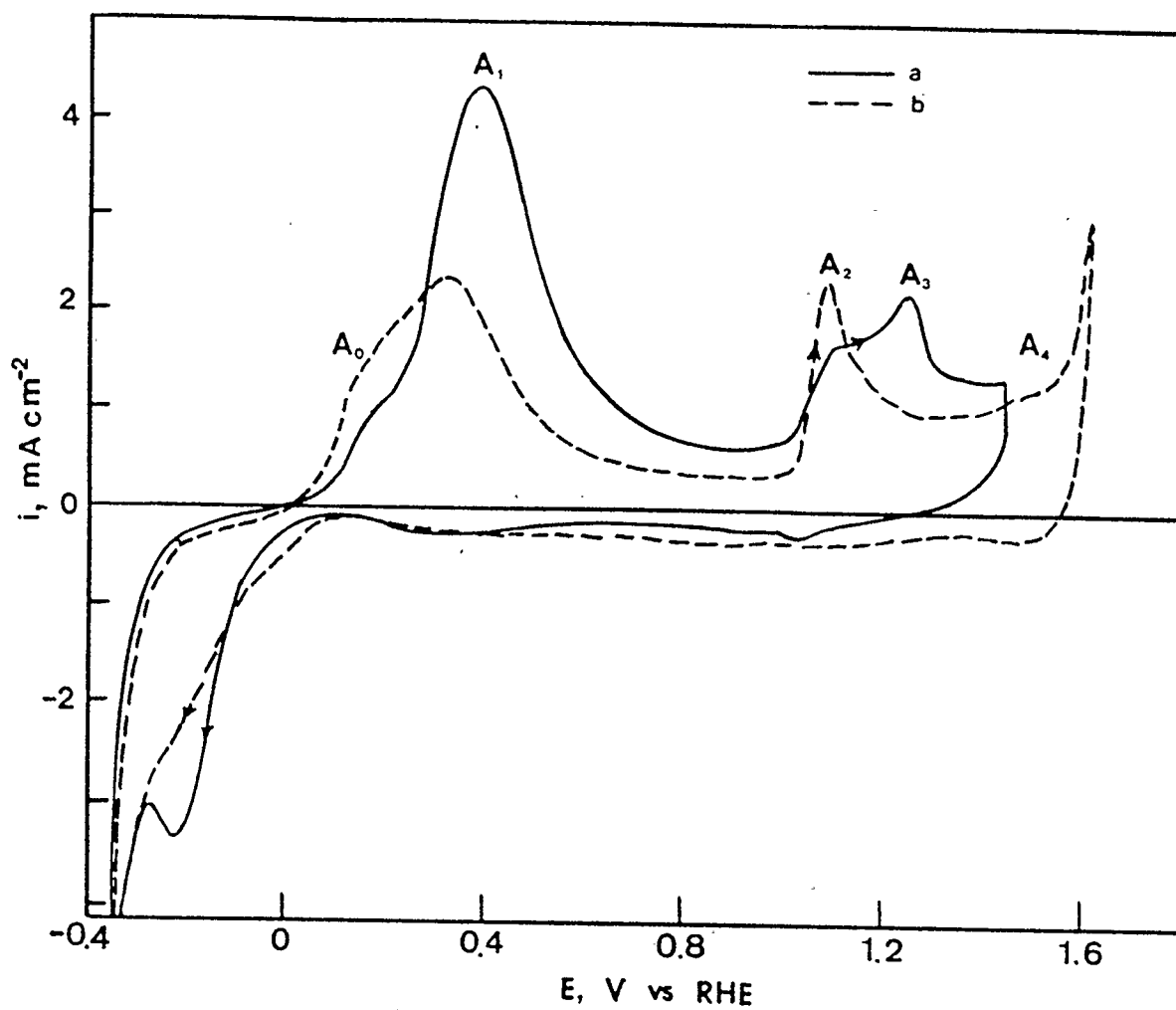


Fig. 4.6a

CVs for polycrystalline Co electrode in 1 M NaOH, $s = 100 \text{ mV/s}$; (curve a) first scan; (curve b) 2nd scan.

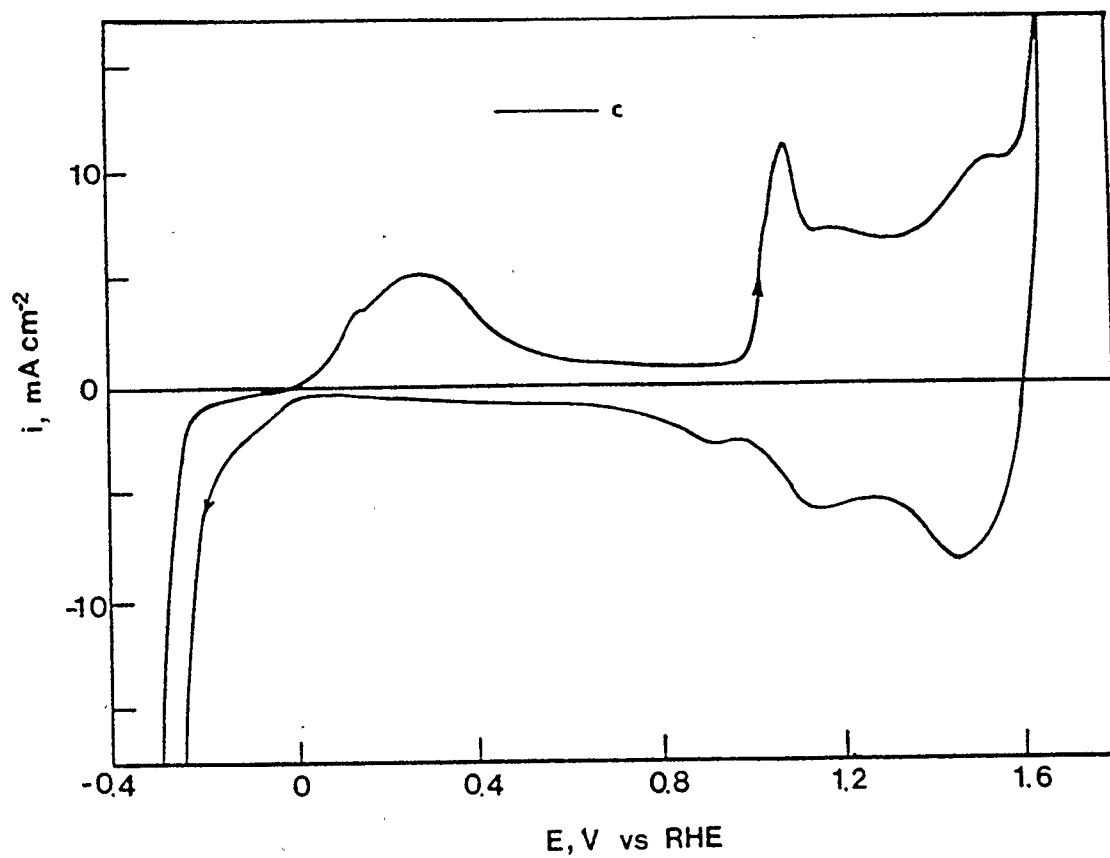
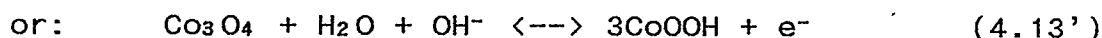
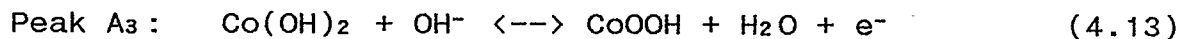
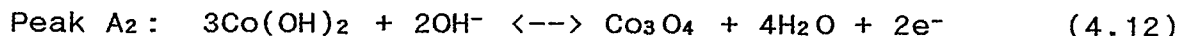
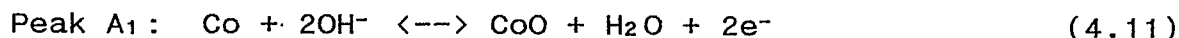
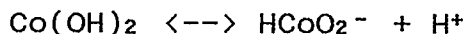
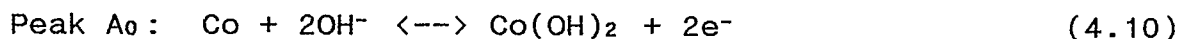


Fig. 4.6b

CV for for Co electrode in 1 M NaOH, $s = 100$ mV/s; (curve c) after 405 min. scan.

to the study of Co electrodes, the anodic peaks in CV may be related to the following reactions:



and vice versa for their reduction counterparts.

There may be other processes than those listed above, which are involved in the oxidation/reduction transition of Co electrodes. According to Behl et al., rotating Co disc experiments showed that cobaltous oxide is slightly soluble in 1-2.5 N KOH solutions, and will be rapidly passivated. Therefore, dissolution is observed only at a very slow scan rate (ca. 5-10 mV/s). Based on this result and under the present experimental conditions, (1 M NaOH, sweep rate = 100 mV/s), dissolution of Co is probably negligible after the first scan of potential.

With repeated potential cycling, the Co electrode is rapidly covered with a brown surface film (possibly CoOOH) which shows electrochromic behavior. Both the anodic and cathodic charges increase with the number of potential cycles (Fig.4.6, curve c). According to Burke, the optimum

potential limits for oxide growth at Co are ca. 0 and 1.2 V (vs. RHE) [71]. Essentially no HER or OER occurs at these limits. This is different from the optimum oxide growth potential limits at Ni electrodes, where $E_{(-)}$ should be ca. -0.5 V, i.e. in the HER range [47]. In the case of Co, the oxide is only partially reduced at $E_{(-)} = 0$ V, so that part of the oxide remains on the electrode surface while the underlying Co metal is oxidized further in the subsequent anodic scan.

By examining the microstructure of our electrochemically formed Co oxide film (Fig.4.7) and comparing it with that at Ni, the former shows a 'mud-cracked' structure. This is the typical hydrous oxide structure observed with other known hydrous metal oxide films [72,102].

Co has been considered as a good catalyst for OER [71]. A 60 mV/decade cd Tafel slope has been reported at low current densities at both Co electrodes [71] and thermally prepared Co_3O_4 spinel oxide electrodes [98]. This comparatively low Tafel slope remains constant to quite high potentials, which is one of the advantages of Co electrodes. Moreover, the Tafel slope appears to decrease to ca. 52 mV/decade cd, if a hydrous Co oxide is formed at the electrode surface by potential cycling [71]. The mechanism of the OER has been proposed to be as follows:

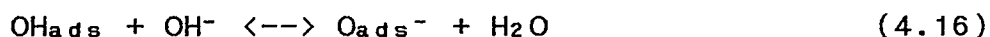
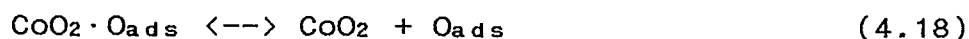




Fig. 4.7

SEM photograph of the oxide film electrochemically formed at Co electrode.



where reaction (4.16) may be the rds at the hydrous oxide free electrode, while a combination of (4.16) and (4.17) might be the rds at a hydrous Co oxide electrode.

Overall, much of the experimental evidence in the literature and obtained in this work indicates that electrochemically formed Co oxides do possess many of the characteristics of hydrous oxides, although no tests regarding their potential/pH dependence have been reported.

A brief study concerning electrochemically co-precipitated Ni-Co electrodes was also carried out in this work in order to provide an understanding whether and how those two elements will influence each other electrochemically. After cathodic deposition, the co-precipitated Ni-Co electrode was subjected to a potential scan (Fig. 4.8, curve a). In comparing Fig. 4.8 (curve a) to Fig. 4.1 for Ni and Fig. 4.6 (curves b and c) for Co, the first CV for the Ni-Co co-precipitated electrode appears very similar to that of Co (Fig. 4.6), except that a relatively higher anodic current and a pair of new peaks appear at 1.31 (A₃) and 1.22 V (C₃), respectively.

During the second potential scan, the reduction peak at -0.03 V disappears. Instead, only HER is observed at the negative limit, which is similar to the behavior of Ni

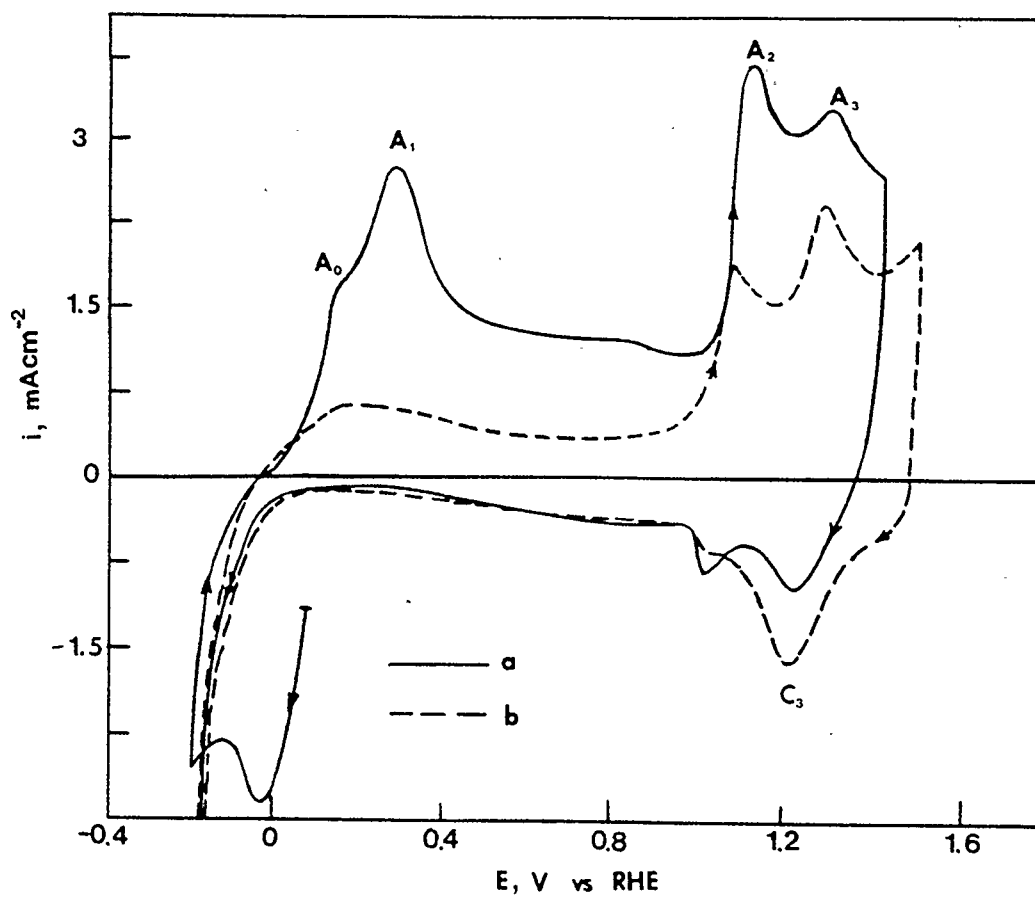


Fig. 4.8a

CVs of co-precipitated Ni-Co electrode in 1 M NaOH, $s = 100 \text{ mV/s}$; (curve a) first scan; (curve b) 2nd scan;

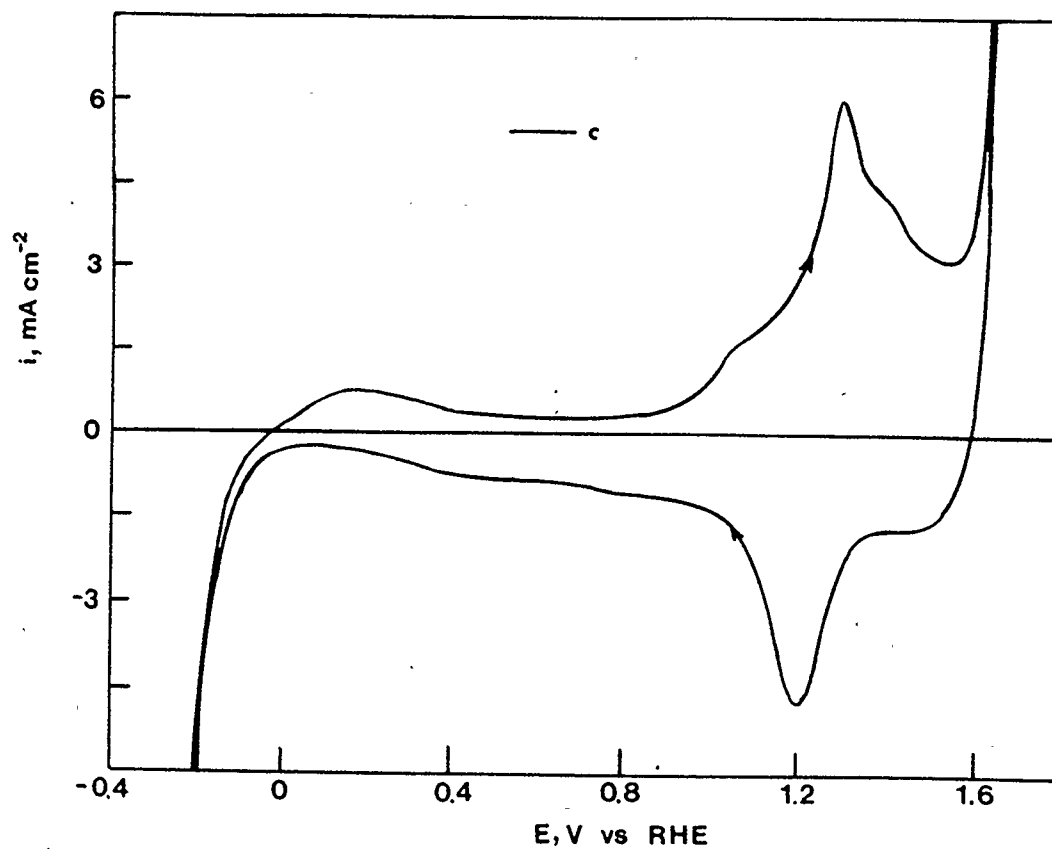


Fig. 4.8b

CV of co-precipitated Ni-Co electrode in 1 M NaOH, $s = 100 \text{ mV/s}$; (curve c) after 60 min. scan.

electrodes under the same experimental conditions. Also, the anodic current drops markedly (Fig. 4.8, curve b). In Fig. 4.8 (curves a and b), the electrochemical behavior of both Ni and Co can be seen. These figures demonstrate the behavior of both Ni and Co.

Although the ratio of Ni:Co is about 2:1 in the electrolyte solution, the response of Co dominates curve a in Fig. 4.8. This may be due to the fact that Co ions diffuse faster than Ni ions within the lattice. According to Wood et al [87], Co oxide forms towards the outside of the oxide, while Ni oxide forms towards the Ni-Co alloy/oxide interface, in a thermally formed Ni-Co oxide film.

It is of interest to note that the anodic current in the first scan is about twice as large as that of the second scan (Fig.4.8, curves a and b). This might be attributed to the oxidation of absorbed hydrogen. It is possible that the electrode absorbs a large amount of hydrogen during the electrodeposition of Ni and Co, which might then be oxidized in the first anodic scan. Other processes such as Co dissolution, or oxidation of Ni and Co to Ni(II) or Co(II) oxides may also be occurring at the surface of the electrode.

Another interesting observation is that peaks A₃ and C₃ become dominant after the first potential scan, while peaks A₂ and C₂ diminish in size with repeated potential cycling (Fig. 4.8, curves b and c). After 60 min. of potential cycling, the charge in peaks A₃ and C₃ were ca. six times

greater than the charge of peaks A₃ and C₃ in Fig. 4.8 (curve b). The appearance of peaks A₃ and C₃ is very much like the principal Ni(OH)₂/NiOOH peaks in Fig. 4.1, although the former are about 120 mV more negative than the peaks at Ni.

A similar result was also obtained by Pickett and Malay [82]. In their work, they considered co-precipitated Co hydroxide as an electrocatalytic agent, which improved the reversibility of the Ni electrochemistry.

After 68 min. of potential scanning, the oxidized co-precipitated Ni-Co electrode was examined by SEM. Fig. 4.9 shows a scanning electron micrograph of the Ni-Co oxide electrode. The smooth appearance of this surface differs from that of oxidized Ni and Co electrodes. In order to determine the homogeneity of the distribution of Ni and Co at this electrode, an x-ray map (Fig. 4.10) was obtained of the area of the surface shown in Fig. 4.9. This map shows that Co is distributed quite evenly. Although it is quite difficult to quantify the ratio of Ni oxide versus Co oxide on the surface, one can conclude that a well-mixed co-precipitated Ni-Co electrode can be obtained by the electrodeposition of the metals, and that the electrode demonstrates a mixture of both Ni and Co electrochemical behavior.

4.3 Electrochemical Behavior of Cr and Mo

A CV of Cr in 1 M NaOH is shown in Fig. 4.11 in which the

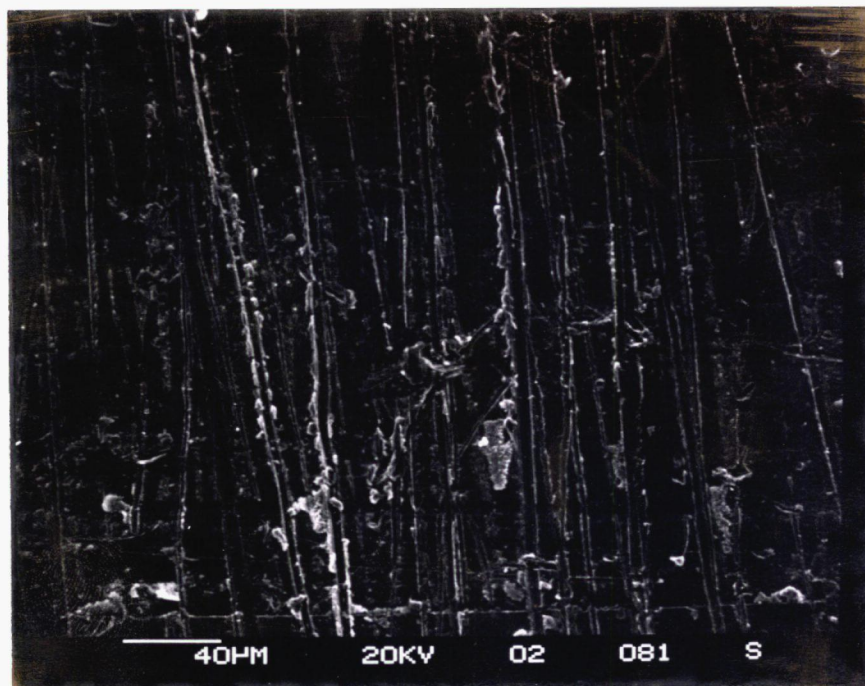


Fig. 4.9

SEM photograph of the oxide film electrochemically formed at coprecipitated Ni-Co electrode.

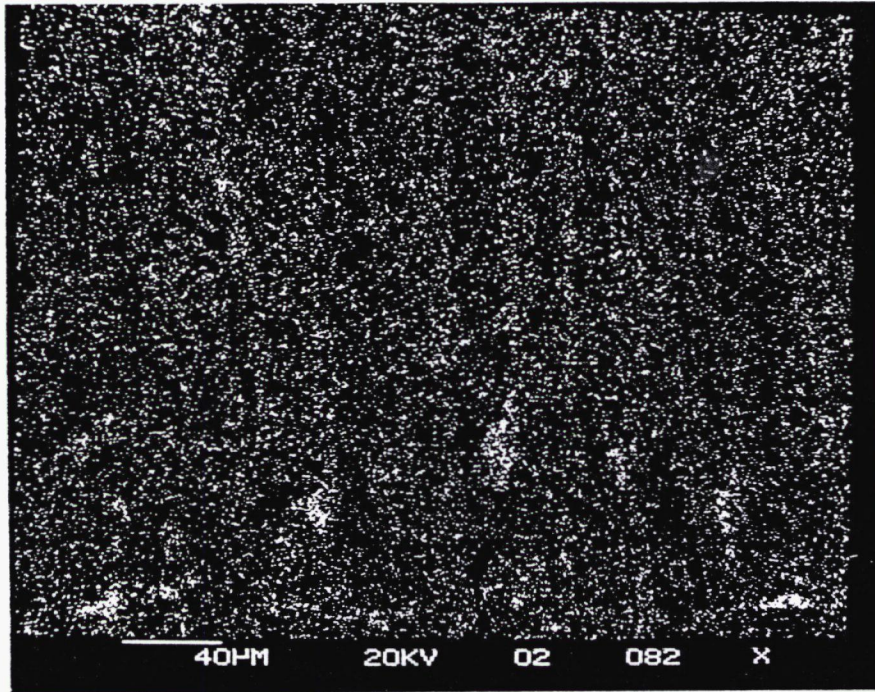


Fig. 4.10 An X-ray map obtained from the same area as shown in Fig. 4.9.

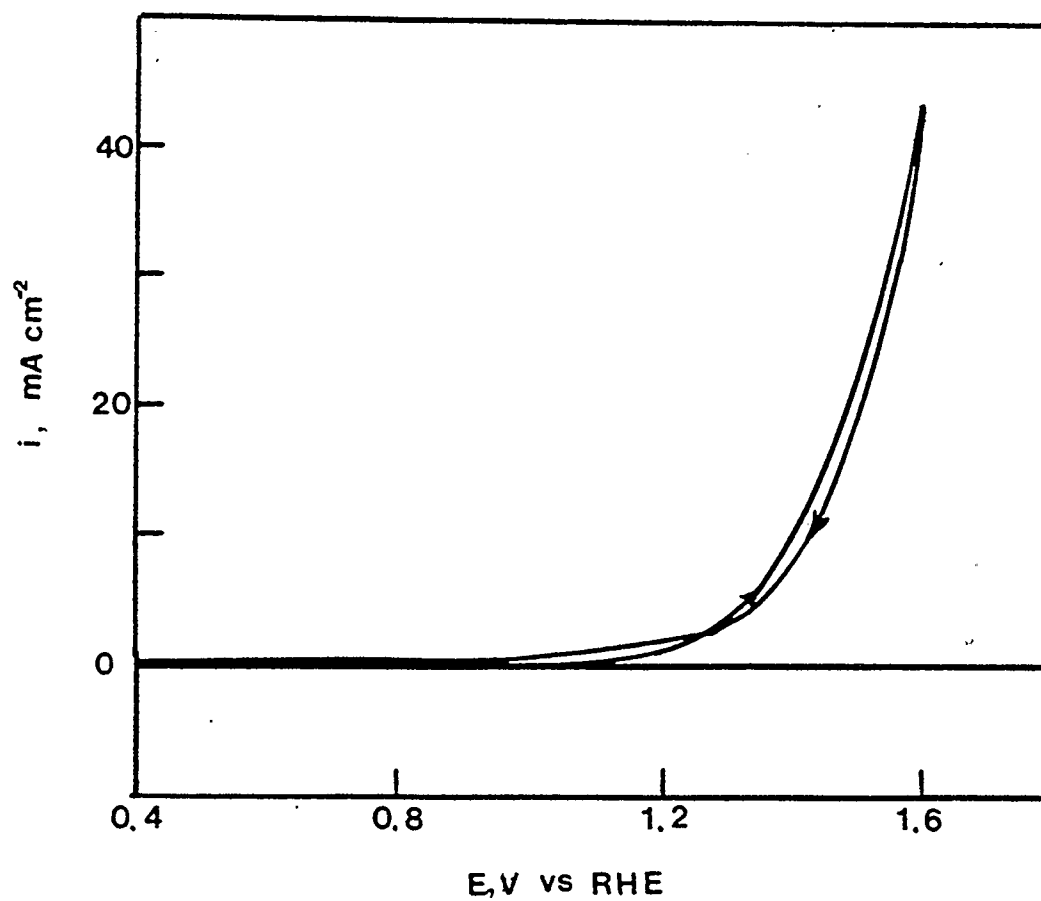


Fig. 4.11 CV for polycrystalline Cr electrode in 1 M NaOH, $s = 100 \text{ mV/s}$.

anodic current rises rapidly at ca. 1.2 V and no reduction process is observed during the cathodic scan. After a few scans, the color of the solution turned yellow. These observations indicate that Cr is being dissolved, probably as CrO_4^{2-} ions [90], under those electrochemical conditions. The yellow solution was analyzed by AA, yielding a strong Cr absorbance. This supports the suggestion [90] that Cr can dissolve readily in high pH solutions. The solution was then kept for the future AAS analyses to compare with solutions in which glassy alloy electrodes were studied (Chapter 5).

Similar experiments were also carried out with Mo electrodes (Fig. 4.12). The anodic current increased rapidly at 0.7 V, probably due to the dissolution of Mo to MoO_4^{2-} , although there is some evidence for passivation at ca. 1.4 V. after several scans, the solution was collected for AAS analysis and Mo was found to be present.

Overall, Ni electrodes show a mixture of behavior. They can thicken oxide with potential cycling and show electrochromic, which are consistent with the behavior of hydrous oxide, but have morphology which is inconsistent with that of hydrous oxides. Co shows more hydrous oxide behavior. For both Ni and Co, the oxide growth rate is relatively slow, and only limited thicknesses are achievable. Both Mo and Cr probably dissolve in 1 M NaOH at positive potentials. Co-precipitated Ni-Co alloy shows the presence of each metal, i.e. shows the behavior of both metals rather than new phase.

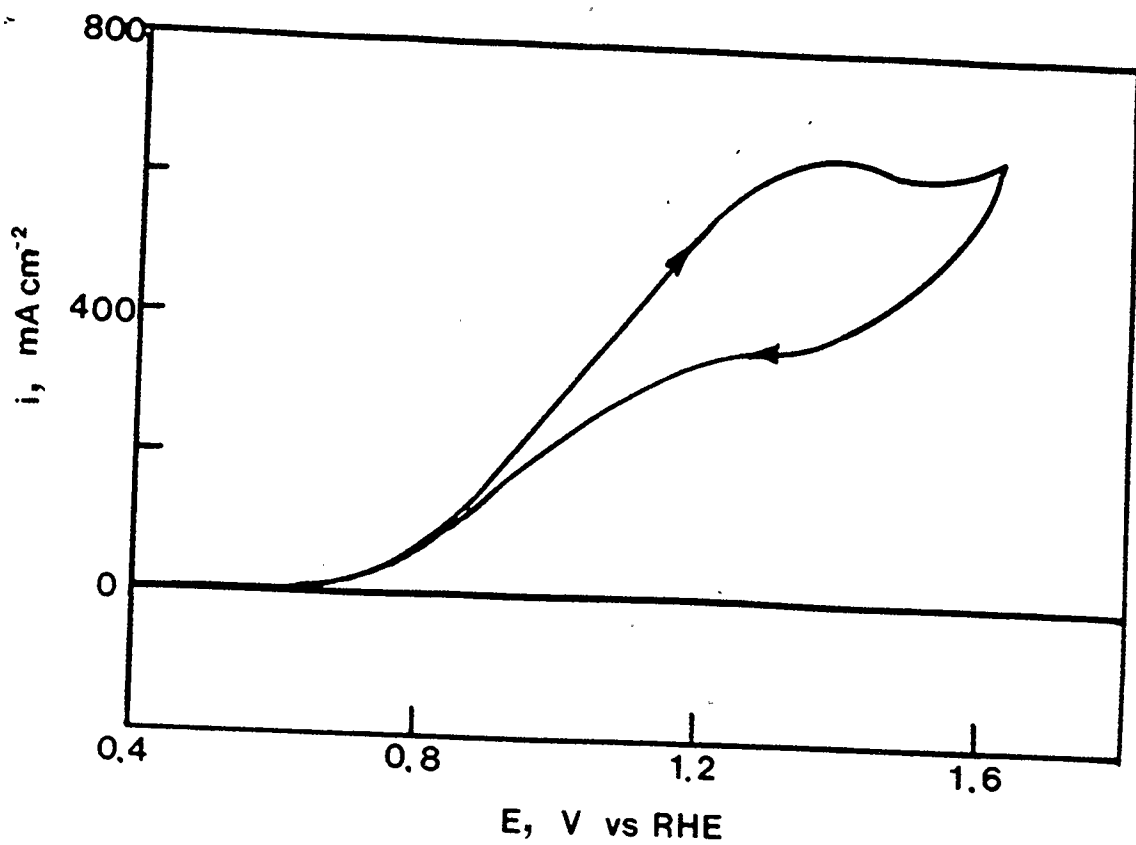


Fig. 4.12 CV for polycrystalline Mo electrode in 1 M NaOH,
 $s = 100 \text{ mV/s}$.

Chapter 5

ELECTROCHEMICAL BEHAVIOR OF "AS-QUENCHED" Ni-Co
GLASSY ALLOYS IN ALKALINE SOLUTIONS

In this chapter, The electrochemical behavior of "as-quenched" Ni-based and Co-based glassy alloys is presented and discussed. The term, "as-quenched" alloys, refers to the alloys which are fresh or have been subjected to one or two potential scans.

5.1 Voltammetric Behavior of Alloy 1 in 1 M NaOH Solution

A typical CV obtained in the first sweep of potential of an "as-quenched" Ni-based glassy alloy (alloy 1) in 1 M NaOH solution is shown in Fig. 5.1 (curve a). Three anodic peaks and one cathodic peak are observed in the potential range between the HER (ca. -0.2 V) and the OER (ca. 1.5 V). The first anodic peak (A_0) is seen more clearly in the inset of Fig. 5.1 at ca. 0.3 to 0.4 V. The second peak (A_1) at about 1.30 V has no corresponding cathodic peak. The third anodic peak (A_2) at about 1.45 V is seen just prior to the OER and has a cathodic counterpart (C_2) at about 1.35 V.

By comparing Fig. 5.1 with Figs. 4.1 and 4.6, peak A_0 is seen at a similar potential to those of the Ni/Ni(OH)₂ and Co/Co(OH)₂ oxidation peaks. It is possible that peak A_0 can be attributed to the formation of either or both Ni(OH)₂ and

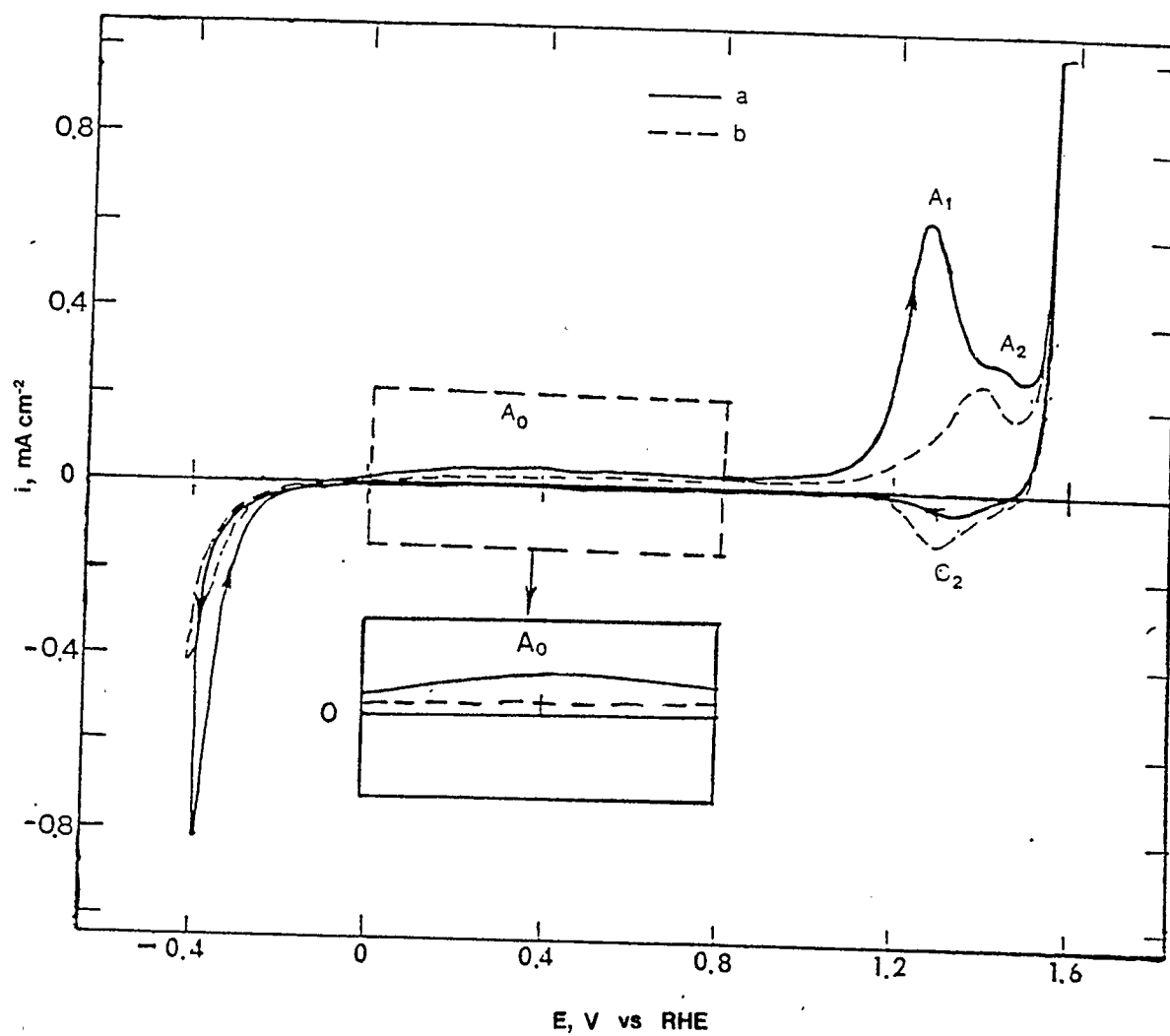


Fig. 5.1

CVs for Ni-based glassy alloy (alloy 1) in 1 M NaOH, $s = 100 \text{ mV/s}$; (curve a) first scan; (curve b) second scan.

Co(OH)_2 formation, and/or to the oxidation of absorbed hydrogen [48]. Peaks A_2 and C_2 are comparable to the oxidation and reduction peaks of Ni(II)/Ni(III) oxide at polycrystalline Ni electrodes (Fig. 4.1), although the peak potentials of the latter are somewhat more negative than those for the glassy alloy (Fig. 5.1, curve a). From the CV of the glassy alloy electrode, Co behavior could not be detected, although Co is present in the oxide film (section 6.1.2). Attempts were made to analyse the solution in which the glassy alloy electrode was subjected to potential cycling for a few hours in order to determine whether the Co in the glassy alloy dissolved into the solution. The result showed no evidence of Co dissolution in this case.

After the first complete sweep in Fig. 5.1 (curve a), the second anodic sweep (Fig. 5.1, curve b) reveals that peak A_1 is now essentially absent, while peaks A_2 and C_2 have moved to slightly negatively, closer to the potential of the Ni(II)/Ni(III) oxide transformation at a Ni electrode (Fig. 4.1). Also, peak A_0 has disappeared (see inset) and the current corresponding to the HER has diminished. The CV of this glassy alloy is now very similar to that obtained at polycrystalline Ni electrodes (Figs. 4.1 and 4.2) except that at the latter, the Ni(OH)_2 peak remains visible and the HER current does not decrease with continuous potential cycling.

In Fig. 5.1 (curve a), it is clear that the total anodic charge (Q_a) of peaks A_1 and A_2 is significantly greater than

that of peak C₂ (Q_c). Also, for a 'fresh' electrode, if the potential is scanned to ca. 1.3 V, just positive of peak A₁, no reduction peak is observed during the cathodic process (Fig. 5.2). These facts, as well as the absence of peak A₁ in the second sweep of the potential, indicate that peak A₁ depicts the permanent stripping of a component of the alloy surface into the solution.

A series of experiments carried out with an "as-quenched" alloy in which E(+) was increased with each cycle of potential is shown in Fig. 5.3. A notable anodic current increase (Fig. 5.3, curve a) is observed at an E(+) of 1.2 V, and no cathodic current is seen. This anodic current decreases with continuous potential cycling to the same E(+) (Fig. 5.3, curve b). When Fig. 5.3 (curve a) is compared with the CVs of polycrystalline Cr and Mo electrode in 1 M NaOH (Fig. 4.10 and 4.11, respectively), a similarity is seen between Fig. 5.3 (curves a and b) and the CV for Cr, in which the dissolution of Cr is observed at ca. 1.1 to 1.2 V.

To further distinguish between Cr and Mo as the principal element being stripped in peak A₁, an Atomic Absorption Spectroscopy (AAS) analysis of solutions, done after scanning the potential of several "as-quenched" alloy electrodes over peak A₁ (as in Fig. 5.2), was carried out. AAS analyses were also performed for solutions obtained from similar studies of the Cr electrode (Fig. 4.10) and for the Co-based glassy alloy (alloy 2) (Fig. 5.9). It was considered necessary to

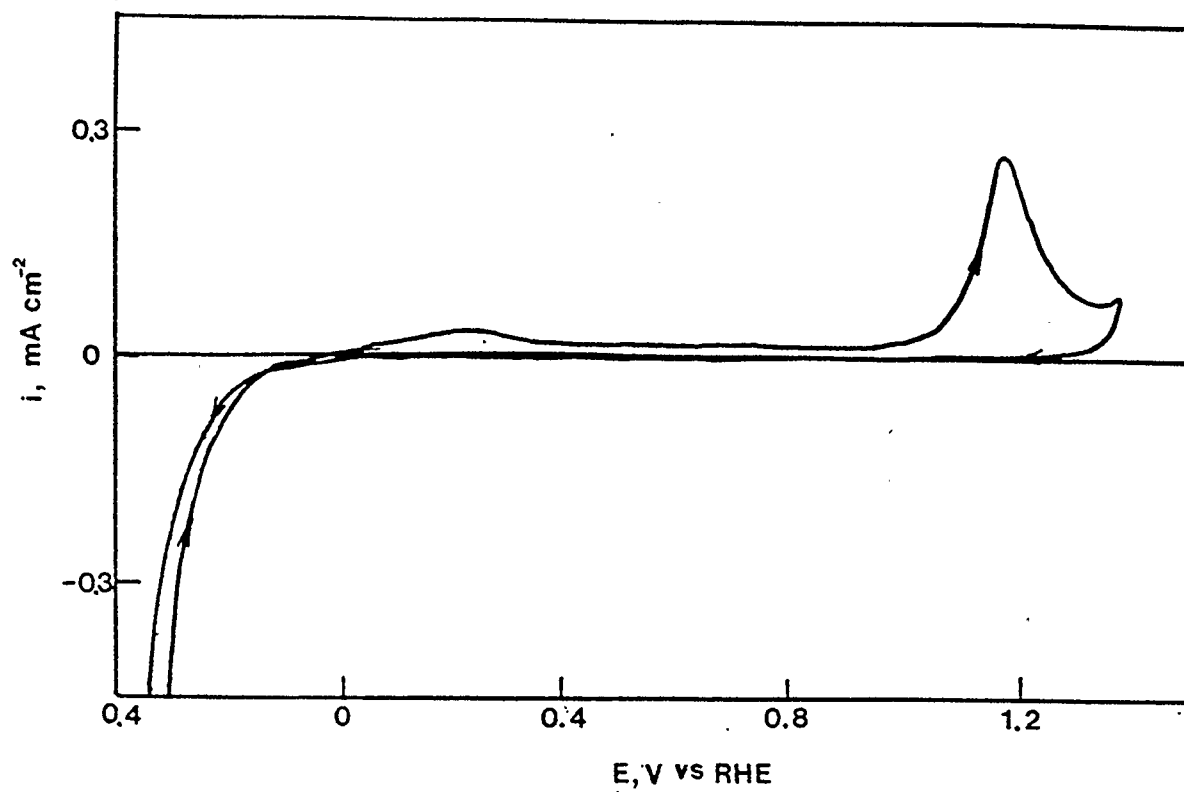


Fig. 5.2 CV for an "as-quenched" alloy 1 in 1 M NaOH, $s = 10 \text{ mV/s}$.

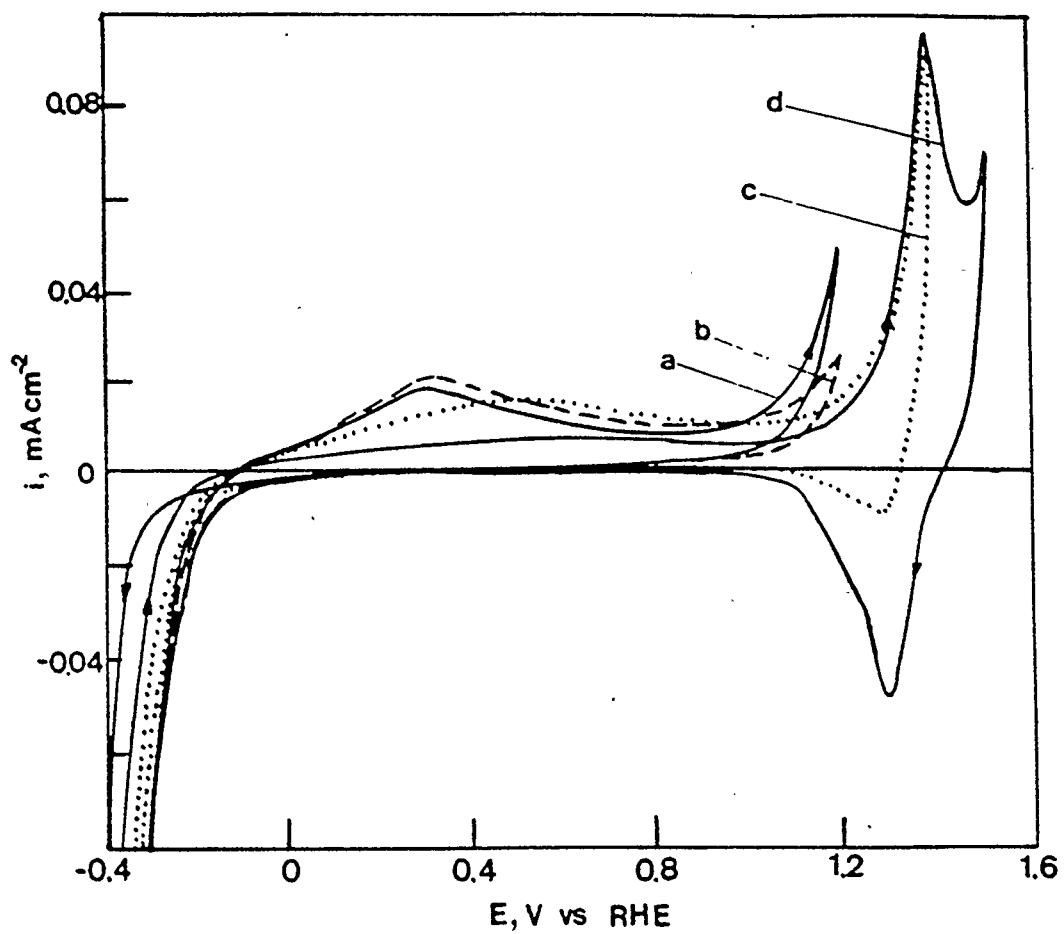


Fig. 5.3 CVs for an "as-quenched" alloy 1 with various $E(+)$ in 1 M NaOH, $s = 10 \text{ mV/s}$.

analyse the solution obtained from alloy 2 (see Section 5.4 for more details), since it has a similar "first-cycle" behavior to that of alloy 1 electrode, but contains a significantly higher percentage of Cr than does alloy 1. Table 5-1 shows the AAS results for these solutions comparison with a "blank" solution of 1 M NaOH. These results indicate that Cr is dissolved from all of these electrodes during potential cycling over A_1 .

According to the above experimental evidence, together with the well known fact that Cr tends to enrich and form a passive film at the surface of these glassy alloy [24,25], one could conclude tentatively that, in alkaline solutions, at relatively oxidizing potentials, these glassy alloys tend to lose the surface-enriched Cr into solution. Therefore, peak A_1 could be attributed to the dissolution of an enriched air-formed chromium oxy-hydroxide film [11,24,25] from the surface of the electrode. The surface analysis results, which will be discussed in Section 5.2, also support this idea.

The cathodic charge density (q_c) obtained from the CVs is considered to be a more accurate measure of the extent of oxide coverage of the electrode than the anodic charge density (q_a) since the anodic peak overlaps significantly with the OER. The q_c during the first potential scan of the "as-quenched" glassy alloy was found to be up to ca. 0.09 mC/cm². During the second potential scan, q_c was ca. 0.15 to

TABLE 5-1

ATOMIC ABSORBANCE ANALYSIS FOR Cr IN VARIOUS
1 M NaOH SOLUTIONS*

<u>Solutions**</u>	<u>Absorbance</u>
blank	0.000
pure Cr	0.357
alloy 1	0.008
alloy 2	0.060

* Flame condition: $\text{N}_2\text{O}/\text{Acetylene}$, (fuel rich).
Instrumental condition: $\lambda = 357.9 \text{ nm}$, HCL*** 6 mA,
bandwidth = 1.0 nm.

** Blank - 1 M NaOH.

Pure Cr - 1 M NaOH solution after electrochemical
oxidation of Cr (Fig. 4.6).

Alloy 1 - 1 M NaOH solution after electrochemical
oxidation of alloy 1 (Fig. 5.2).

Alloy 2 - 1 M NaOH solution after electrochemical
oxidation of alloy 2 (Fig. 5.4).

*** Hollow cathode lamp.

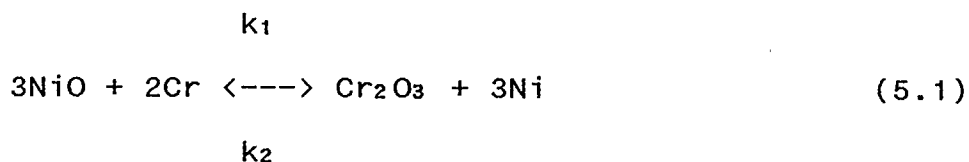
0.25 mC/cm². These values are of the same order as the charge densities of one monolayer oxide formation at many metal electrodes [69,103].

It is very difficult to determine how much charge is equivalent to one monolayer of oxide at the glassy alloy electrode and, inversely, how many monolayers of oxide are involved in peaks A₂ and C₂, because the electrochemical processes during the first few potential scans are complicated by the electrodisolution of enriched Cr (and probably Mo). In addition, the composition and density of the oxide and the true surface area of the electrode are not known. In this work, the q_c in peak C₂ during the second potential scan was used as a reference (q_i) against which subsequent charges are given. q_i is probably not much influenced by the electrodisolution reactions. The roughness factor of the glassy alloy is not available, but could readily be 1.5 to 2.0.

However, the q_i on Ni electrodes during the first potential cycle was found to be between 3 and 5 mC/cm², which is ca. 20 times larger than that at the glassy alloy. Although the roughness factor of a mechanically polished Ni electrode may be 2 to 3, it is apparent that five to ten monolayers of NiOOH oxide form during the first potential scan at Ni. In this respect, Ni and Ni-based glassy alloy behave quite differently.

5.2 XPS, AES and SEM Analyses of Alloy 1

The XPS study of the "as-quenched" alloy 1 showed that a Cr-enriched oxide film (mainly Cr_2O_3 or $\text{Cr}(\text{OH})_3$) was present on the surface of the alloy, which supports the conclusion drawn from the voltammetric result in Section 5.1, as well as prior reports [18,90]. In contrast, Ni and Co are found to be less concentrated on the alloy surface than in the bulk, and are predominantly in the metallic state. This could be explained by the occurrence of the following reaction in air, using Ni to represent either Ni or Co:



As Cr oxide is thermodynamically more stable than the oxides of Ni and Co [99], k_1 is much greater than k_2 , and therefore it could be said that the presence of Cr at the surface 'protects' Ni and Co from oxygen.

Another important observation is that boron is also enriched (ca. 7.2%), in the form of B_2O_3 , on the surface of the "as-quenched" electrode, although the total percentage of B in the alloy is only 3.5%. This tendency is consistent with the results reported by Hashimoto et al [7]. In their work, B was found to be present in the surface film as chromium borate which, to some extent, reduces the amount of hydrated chromium oxy-hydroxide film on the surface. Table 5-2 shows a comparison of the XPS-determined "as-quenched"

TABLE 5-2

XPS-DETERMINED COMPOSITION* OF THE "AS-QUENCHED"
NI-BASED GLASSY ALLOY

<u>Element</u>	<u>Depth into Sample**</u>	
	<u>10 Å</u>	<u>200 Å</u>
Ni	28.0	43.0
Co	10.5	23.5
Cr	18.0	8.5
Mo	6.0	14.0
Fe	2.5	3.0
B	5.0	3.0
O	23.0	2.5
C	7.5	3.0

* Weight %.

** Ar ion etching.

alloy 1 composition after Ar ion etching to 10 Å and 200 Å below the original surface.

An AES depth profile of the "as-quenched" alloy 1 is shown in Fig. 5.4, from which the differences between the composition of the surface and bulk of this alloy can be clearly seen. Both XPS and AES results support the idea that Cr tends to enrich at the alloy surface, although the concentration of Cr in this case is relatively lower than the literature values [11-14] obtained from similar glassy alloys. Moreover, it is seen that the concentration of Mo is relatively low at the surface, but higher in the bulk of the alloy, which is also consistent with the results reported by Hashimoto et al [7,12].

The SEM analyses provided some information about the microstructure of this glassy alloy. Fig. 5.5 shows a scanning electron micrograph of the "as-quenched" glassy alloy surface, which reveals a smooth and noncrystalline morphology. The composition of this alloy was determined by x-ray analysis (Fig. 5.6).

5.3 HER and OER at Alloy 1 in 1 M NaOH Solution

The Tafel behavior of the HER at an "as-quenched" alloy 1 has also been studied in this work. This was done in order to compare the electrochemical activity of this fresh alloy surface with the oxidized surface (see Section 6.1.3). Also, by comparing curves a and b in Fig. 5. 1, it is obvious that

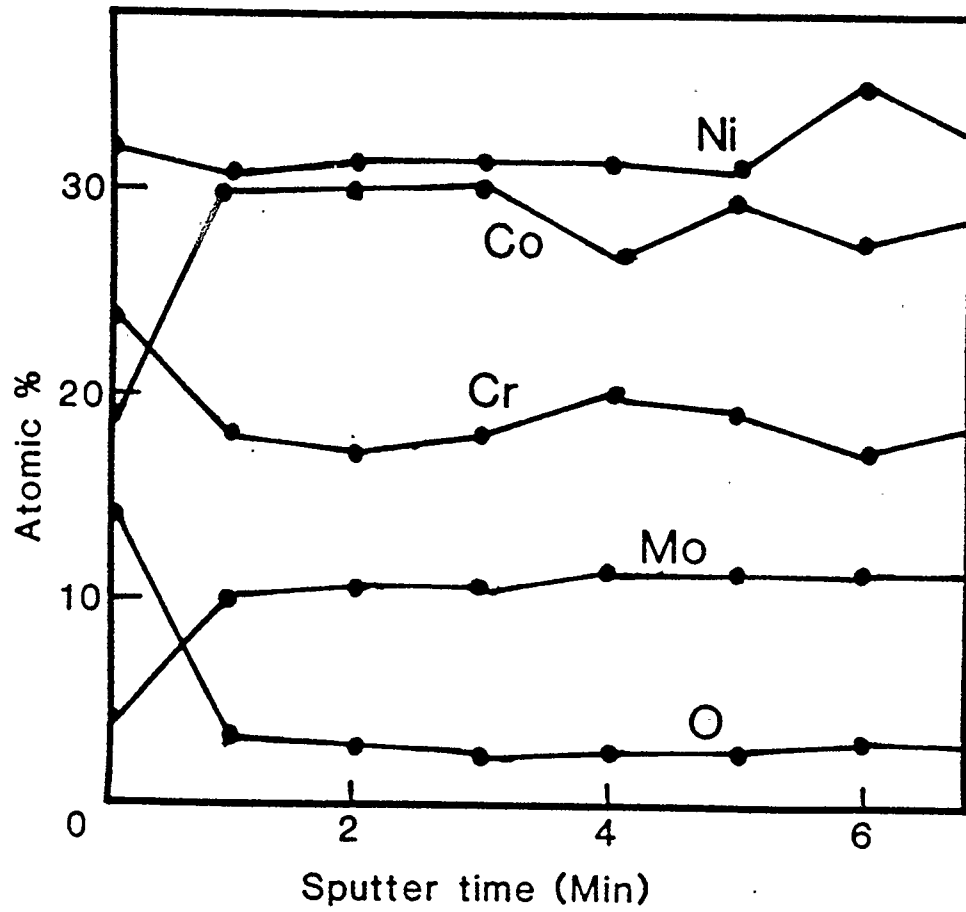


Fig. 5.4 AES depth profile of an "as-quenched" alloy 1.

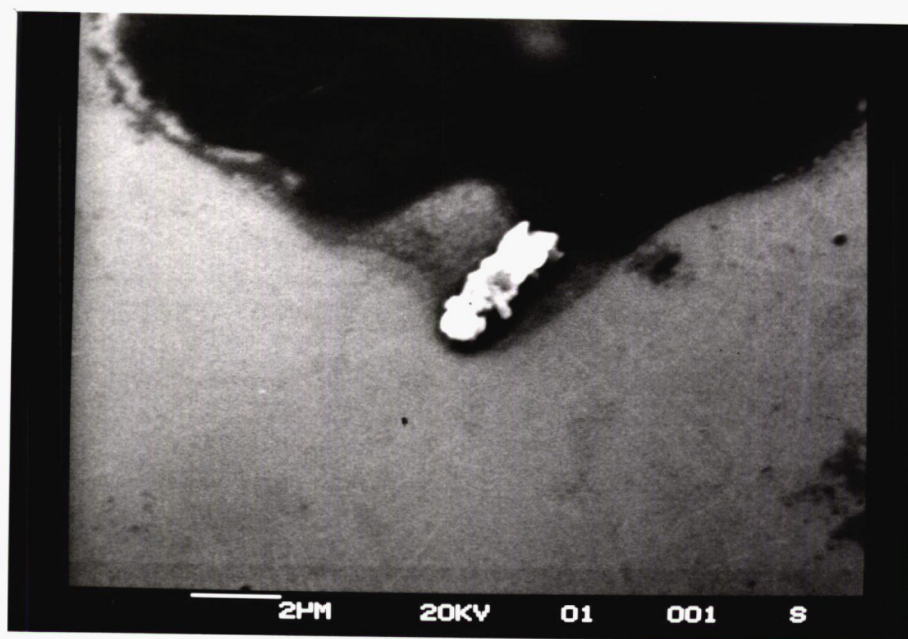


Fig. 5.5 SEM photograph of an "as-quenched" alloy 1 surface.

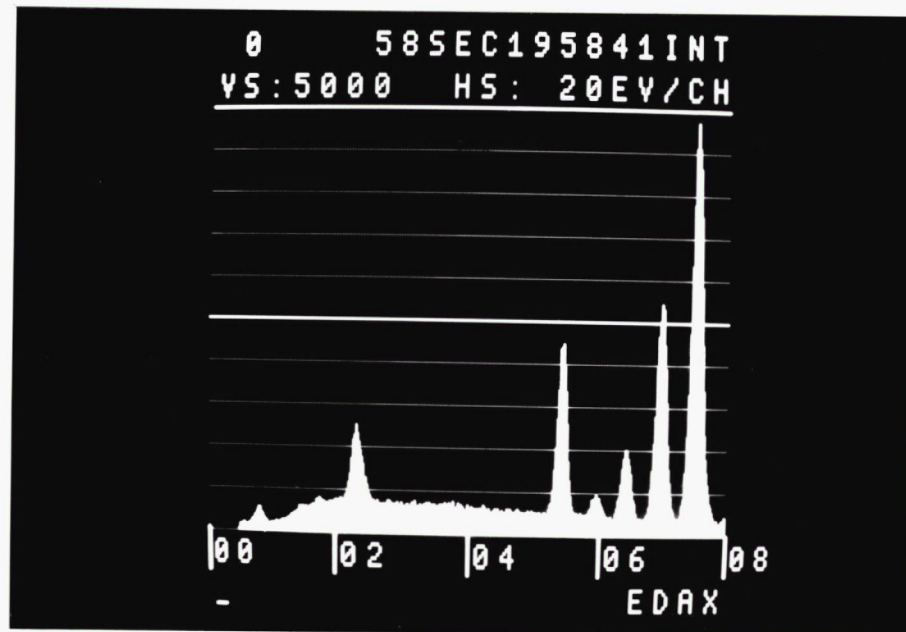


Fig. 5.6 The composition of the "as-quenched" alloy 1, as determined by X-ray analysis.

the currents corresponding to the HER in the second scan of the potential are remarkably decreased vs. those at an "as-quenched" electrode.

A Tafel plot for the HER at the "as-quenched" alloy 1 is shown in Fig. 5.7. A Tafel slope of ca. 120 mV/decade cd. was obtained in the potential range of 0.0 to -0.45 V. This is very close to the reported Tafel slope on similar alloys and related metals in various alkaline solutions [28,92,93]. At the surface of the "as-quenched" glassy alloy, the results of XPS and AES have shown the composition to be mainly Ni and Co metal and Cr oxide. It is not clear which element is dominant in the HER reaction, although it is possible that the overall surface behaves most like Ni in the HER.

The 120 mV Tafel slope could be explained by a mechanism similar to that involved in the HER at a Ni electrodes presented in Chapter 4. Extrapolation of the plot to 0.0 V gives an exchange current density, i_0 , of ca. 2.5×10^{-6} A/cm², which is comparable to the values reported by other authors [28].

The kinetics of the OER at the glassy alloy electrode have also been briefly investigated in this study. At the "as-quenched" alloy electrode, the Tafel slope for the OER is ca. 44 mV/cd (Fig. 5.8) in the potential range from 1.48 to 1.60 V. Above 1.60 V, there is another Tafel region which may be related to diffusion controlled oxygen evolution; no attempt was made to study this reaction at these high

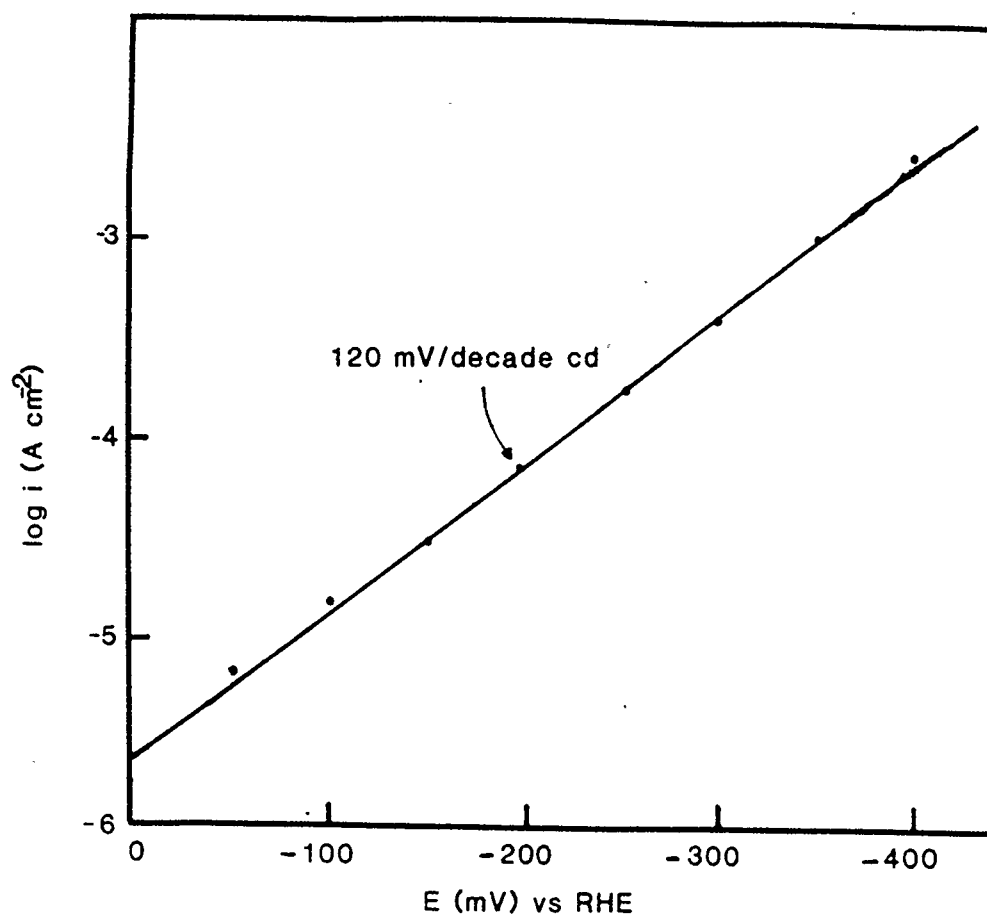


Fig. 5.7 Tafel plots for the HER at "as-quenched" alloy 1.

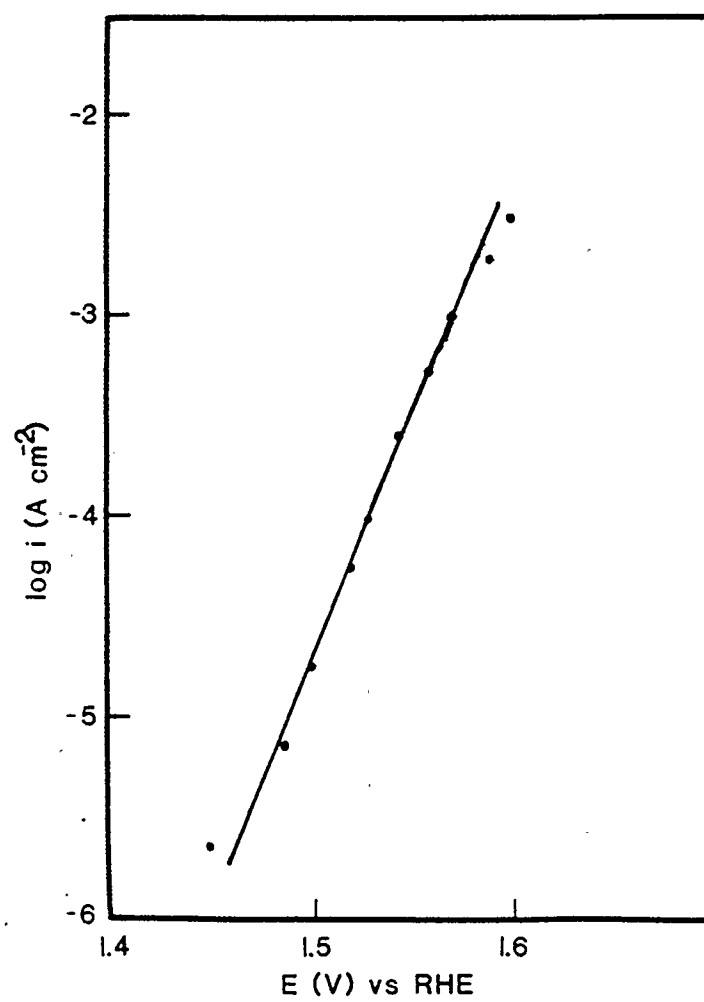


Fig. 5.8 Tafel plots for the OER at "as-quenched" alloy 1.

potentials. The 44 mV/cd Tafel slope falls between the values of the slopes obtained at Ni and at Co electrodes [53,71,89,95] in similar solutions. Therefore, it is possible that the OER is occurring at a surface composed of a mixture of Ni and Co oxide, since both Cr and Mo should have dissolved at lower potentials.

5.4 The Electrochemical Behavior of "As-Quenched" Alloy 2 in 1 M NaOH Solution

A brief study of the Co-based glassy alloy (alloy 2) was also carried out for comparison with the Ni-based glassy alloy (alloy 1). Fig. 5.9 (curves a and b) depicts the first and third cycle of potential of the "as-quenched" alloy 2 electrode.

During the first anodic scan (curve a), three anodic peaks at 0.6, 0.85 and 1.32 V (vs. RHE) and one broad cathodic peak at 0.78 V are observed. For the first two anodic peaks, no corresponding cathodic peaks are observed; these two anodic peaks are not present in the second and subsequent anodic scans. It is possible that these peaks are related to the electrodisolution of Co, W or adsorbed organics.

It is of interest to note that the peak at 1.32 V (peak A₃) appeared at a somewhat similar potential to peak A₁ (alloy 1) in Fig. 5.1 (curve a). In the latter, peak A₁ was considered to be related to the anodic dissolution of Cr. By

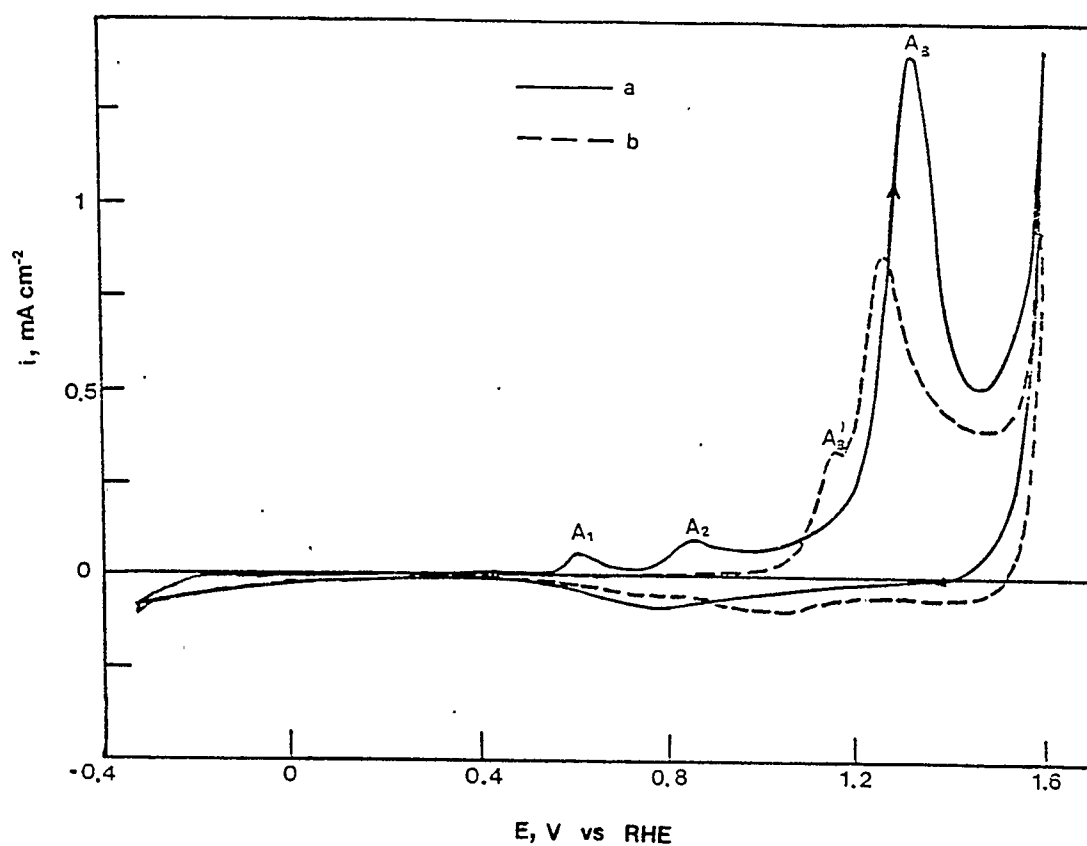


Fig. 5.9

CVs for an "as-quenched" Co-based glassy alloy (alloy 2) in 1 M NaOH, $s = 100 \text{ mV/s}$, (curve a) first scan; (curve b) 3rd scan. Current sensitivity in curve b is half of that in curve a.

examining the CV of the third potential scan (Fig. 5.9, curve b), the peak potential of A₃ was shifted negatively and its magnitude increased relatively to curve a (Fig. 5.9). By comparing Fig. 5.9 with the CVs obtained with a Cr (Fig. 4.11) and alloy 1 electrode (Fig. 5.1), peak A₃ appears to be related to Cr dissolution. This has been proved by solution analysis by AAS.

The most important conclusion to be obtained from this chapter is that Cr is enriched on the surfaces of both "as-quenched" alloy 1 and 2, but dissolves at positive potentials. Also, the CVs of "as-quenched" alloy 1 appear similar to those of Ni electrodes but have much smaller q_i .

Chapter 6

ELECTROCHEMICAL OXIDATION AND BEHAVIOR OF OXIDIZED GLASSY ALLOYS

6.1 General Description

6.1.1 Electrochemical Oxidation of Alloy 1 in 1 M NaOH Solution

With repeated potential cycling of the glassy alloy electrode from a potential negative of peak C₂ to potentials just into the range of the OER, the shape and potential of peaks A₂ and C₂ changed gradually (Fig. 6.1, curves a and b). Also, the magnitude of this pair of peaks clearly increased with time of potential cycling, while the current flowing at potential negative of C₂ did not increase and even decreased somewhat in the potential range of the HER.

As peaks A₂ and C₂ increased with potential cycling, the electrode surface was seen to be electrochromic, being darker at potentials positive of A₂ and lighter at potentials negative of C₂. Furthermore, with the increase in magnitude of peaks A₂ and C₂, the color of the electrode surface changed, a manner similar to the development of interference colors with increasing film thickness [100]. This was not observed with either Ni or Co electrodes under the same experimental conditions.

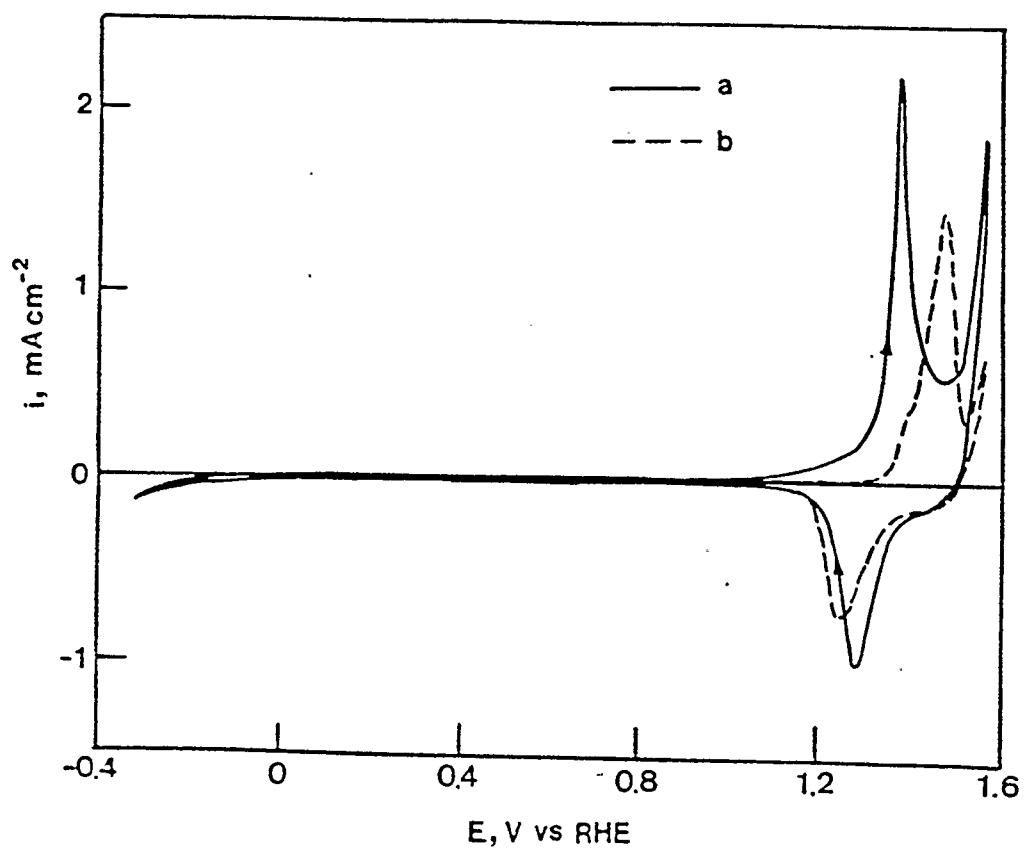


Fig. 6.1 CVs for oxidized glassy alloy electrode, $s = 100$ mV/s; (curve a) the 6th scan; (curve b) after 60 min. scan. The current scale in curve b is 10 times less sensitive than in curve a.

The ratio of Q_t/Q_i (Q_t = charge in peak C_2 at time t ; Q_i = charge in peak C_2 in second scan) was used to represent the extent of oxide coverage after t minutes of potential cycling. The relationship of this charge ratio to the color of the electrode surface is shown in Table 6-1. It is seen that the same color could be repeatedly observed at different oxide thicknesses and that the final color of dark brown was seen after 110 min of potential cycling under these experimental conditions.

By comparing Fig. 6.1 (curves a and b) with the CVs obtained at polycrystalline Ni (Fig. 4.1), Co (Fig. 4.6) and Ni-Co co-precipitated alloy (Fig. 4.10) electrodes, it can be seen that the appearance of the CV of the alloy 1 is very similar to that of the Ni electrode, but quite different from those of Co and co-precipitated Ni-Co alloy electrodes. In the case of Ni-Co co-precipitated alloy, the oxidation and reduction behavior of both Ni and Co could be distinguished on the CV.

6.1.2 XPS, AES and SEM Analyses of Electrochemically Oxidized Alloy 1

SEM analyses were carried out on glassy alloy 1 electrodes which had been subjected to potential cycling for various lengths of time. Generally, the electrochemically oxidized electrodes have a 'mud-cracked' type of morphology (Fig. 6.2), which is the typical microstructure seen for

TABLE 6-1

OXIDE GROWTH IN RELATION TO COLOR
OF ELECTRODE SURFACE

<u>TIME (min.)*</u>	<u>Q_t/Q_i</u>	<u>COLOR</u>
1	1	silver white**
5	5.7	silver (darker)
10	10.2	yellowish silver
15	13.1	yellow
20	16.4	light brown
30	26.3	brown
40	33.3	light purple
45	37.5	blue
50	39.9	light blue
60	49.1	greenish silver
65	53.4	yellow
70	55.8	golden brown

* Continuous cycling at $s = 300 \text{ mV/s}$, $E_{(+)} = 1.6 \text{ V}$, $E_{(-)} = -0.4 \text{ V}$, 1 M NaOH .

** Original color of the glassy alloy.

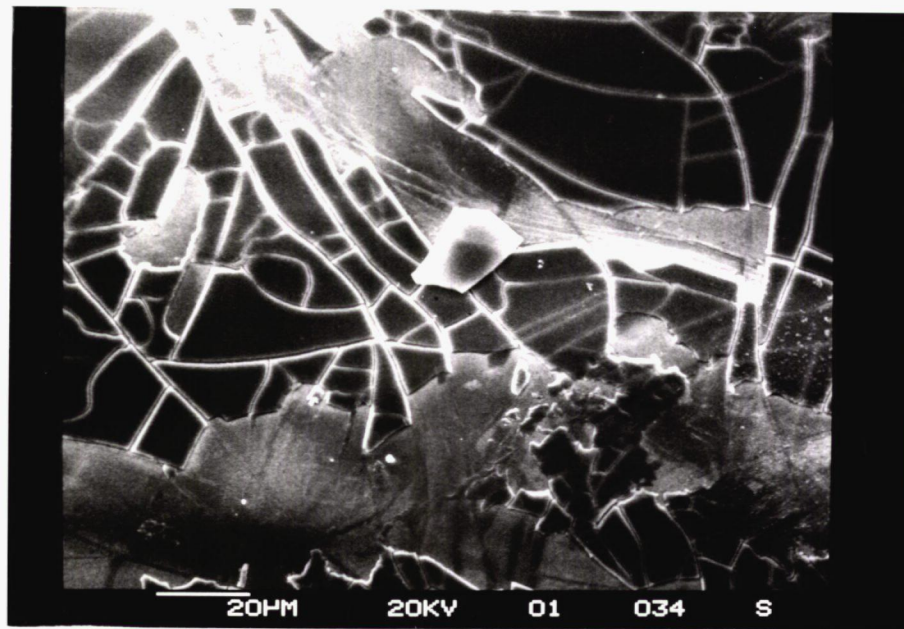


Fig. 6.2 SEM photograph of fractured oxidized electrode surface (Q_t/Q_i is ca. 120).

hydrous oxide films formed electrochemically at electrodes such as Ir etc. [72,102].

In comparison with electromicrographs of electrochemically oxidized polycrystalline Ni (Fig. 4.5), Co (Fig. 4.7) and Ni-Co co-precipitated alloy (Fig. 4.10) electrodes, the oxidized alloy 1 (Fig. 6.2) shows a much smoother surface. Also, the 'mud-cracked' structure at the oxidized alloy 1 is seen only at an oxidized Co electrode, but the latter shows a lesser extent of this kind of structure.

By carefully examining cross-sections of these glassy alloy electrodes (Fig. 6.3 and 6.4), oxide film thicknesses could be correlated with their Q_t/Q_i ratios (Fig. 6.5). The curvature in Fig. 6.5 is an indication that for thick oxide films at high sweep rate ($s = 100$ mV/s), the reaction is not at equilibrium so that less than the complete oxide charge can be measured in the CVs. However, this figure is still useful to estimate the oxide film thickness from the measured Q at 100 mV/s.

XPS and AES, along with Ar ion sputtering methods, were also used to determine the oxide film composition and comparative thicknesses. These were found to agree closely with those predicted from Fig. 6.5, although the sputtering rate for this particular Ni/Co oxide is not known, so that the true oxide film thickness could not be determined. Fig. 6.6 shows a depth profile of the oxidized glassy alloy obtained by AES. It is seen that the percentage of Cr and Mo

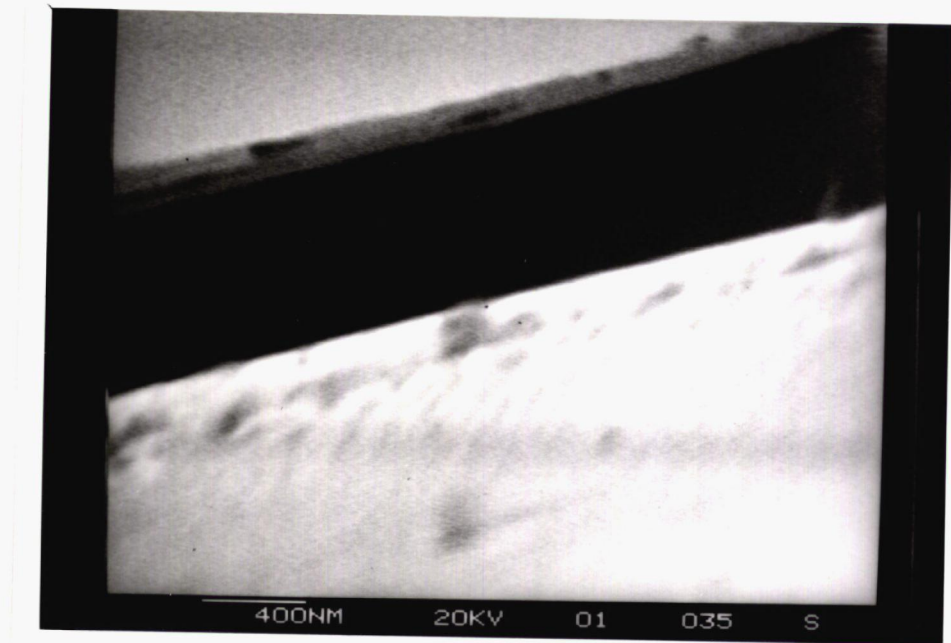


Fig. 6.3 SEM photograph of cross-section of oxide film shown in Fig. 6.2; Q_t/Q_i is ca. 120.

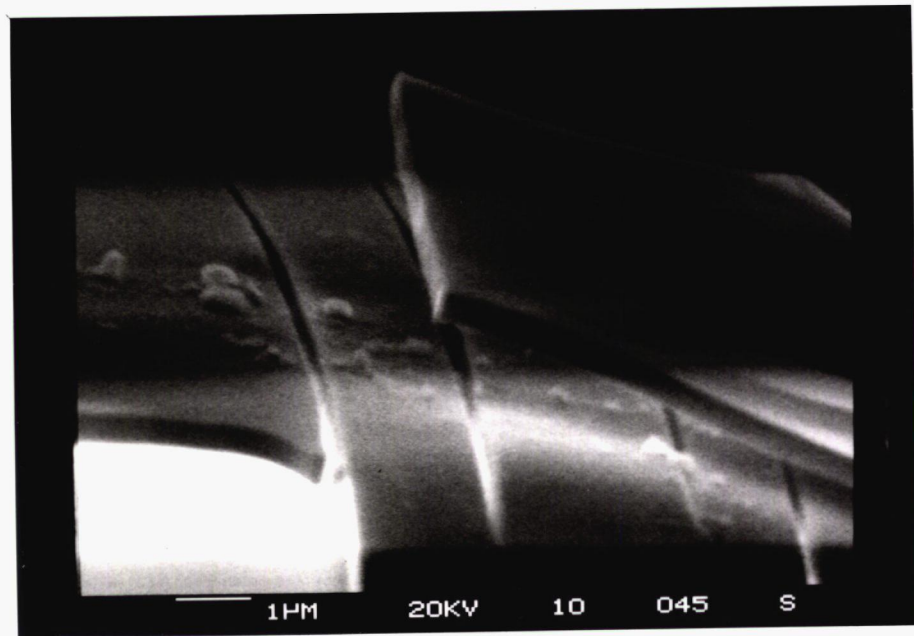


Fig. 6.4 SEM photograph of cross-section of oxide film;
 Q_t/Q_i is ca. 98.

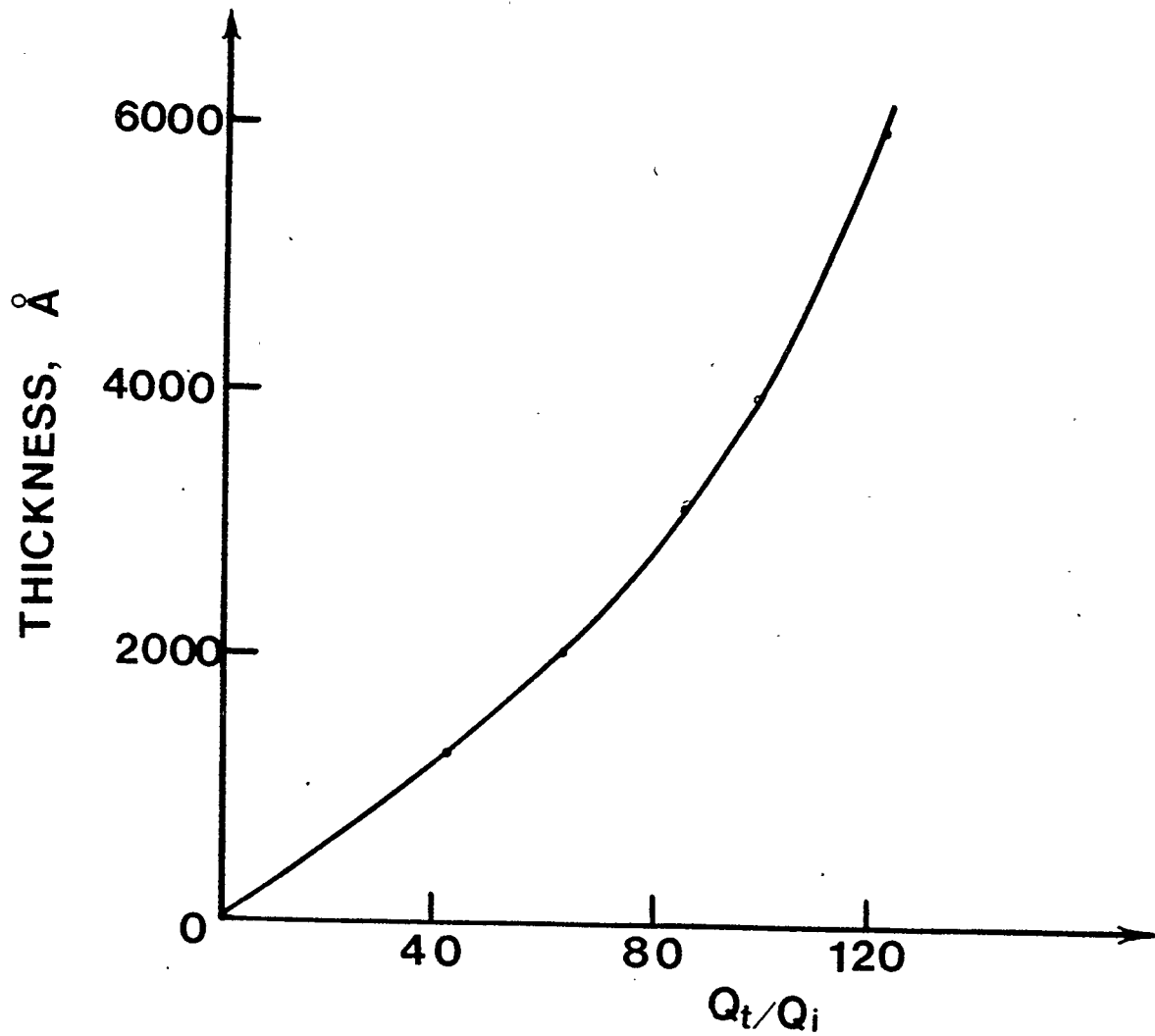


Fig. 6.5 Thickness of oxide film from SEM vs. Q_t/Q_i , $s = 100$ mV/s.

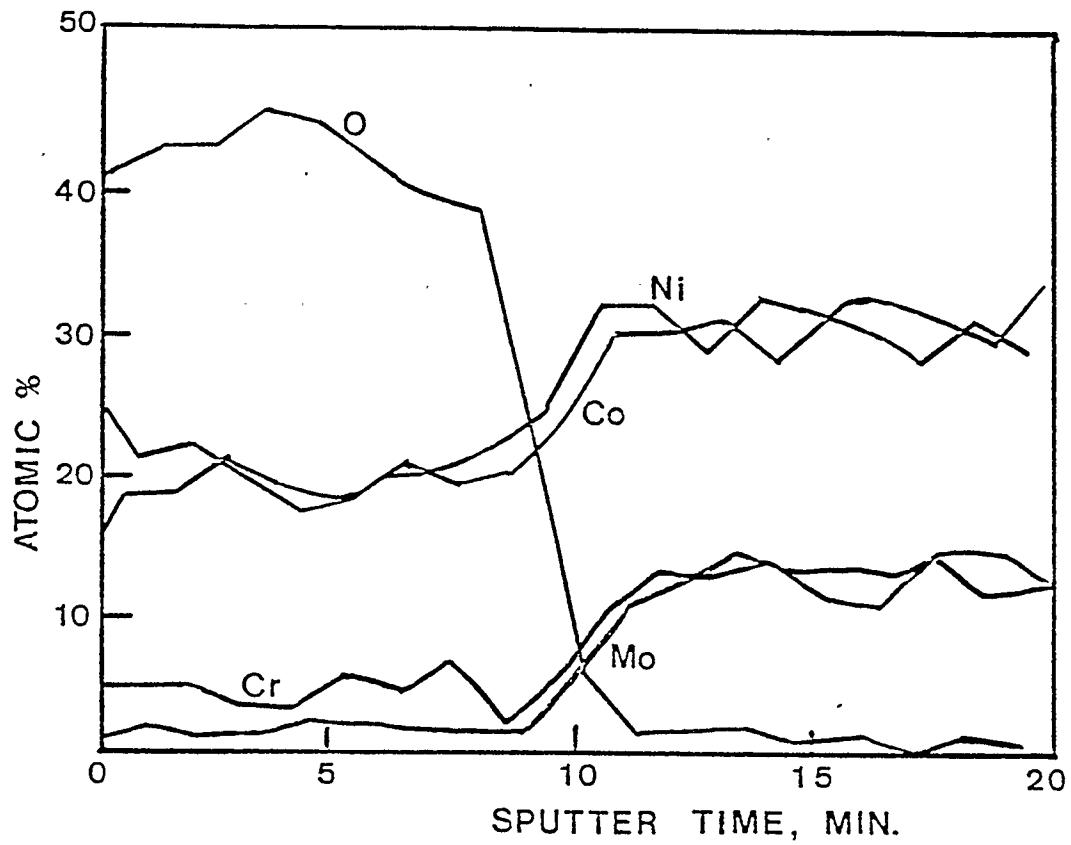


Fig. 6.6 AES depth profile of an oxide film; Q_t/Q_i is ca. 52.

present is lower in the oxide than in the underlying metal. This supports the conclusion of Chapter 5 that, in this glassy alloy, only Ni and Co are oxidized and reduced, while Cr and Mo dissolve under these experimental conditions.

The results obtained from XPS are in agreement with those from AES. The occurrence of some "charging" during XPS analysis was observed, perhaps indicative of poor electronic conductivity of this oxide film when it is dried out in the vacuum chamber.

When the electrode potential was held at positive values (e.g. 1.55 to 1.60 V) before the XPS and AES analyses, a significant amount of Na was detected at a constant level throughout the oxide film by XPS (Fig. 6.7). This will be discussed in detail in section 6.3.

6.1.3 HER and OER at Oxide-Covered Alloy 1 Electrode

A Tafel plot for the HER on an oxidized alloy with a thickness of ca. 700 Å is shown in Fig. 6.8. Three different Tafel regions were observed. At low overpotentials (up to ca. -150 mV), a steady-state current density of ca. 1.7×10^{-6} A/cm² was observed. When an overpotential greater than -150 mV was applied, a slope of 120 mV/decade cd was observed, as in the case of an "as-quenched" glassy alloy. When the overpotential was increased further to ca. -300 mV or more, the current density began to increase rapidly with time at each potential. A steady-state current could not be

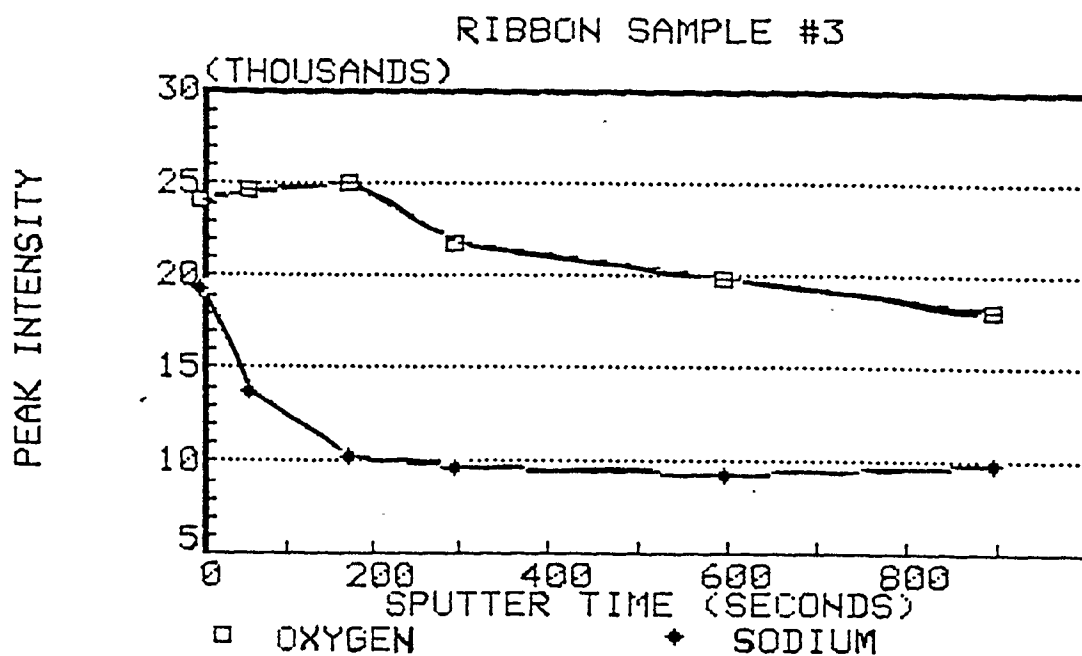


Fig. 6.7 Depth profile of Na and O obtained from XPS analysis; oxide formed in 1 M NaOH, Q_t/Q_i is 73.

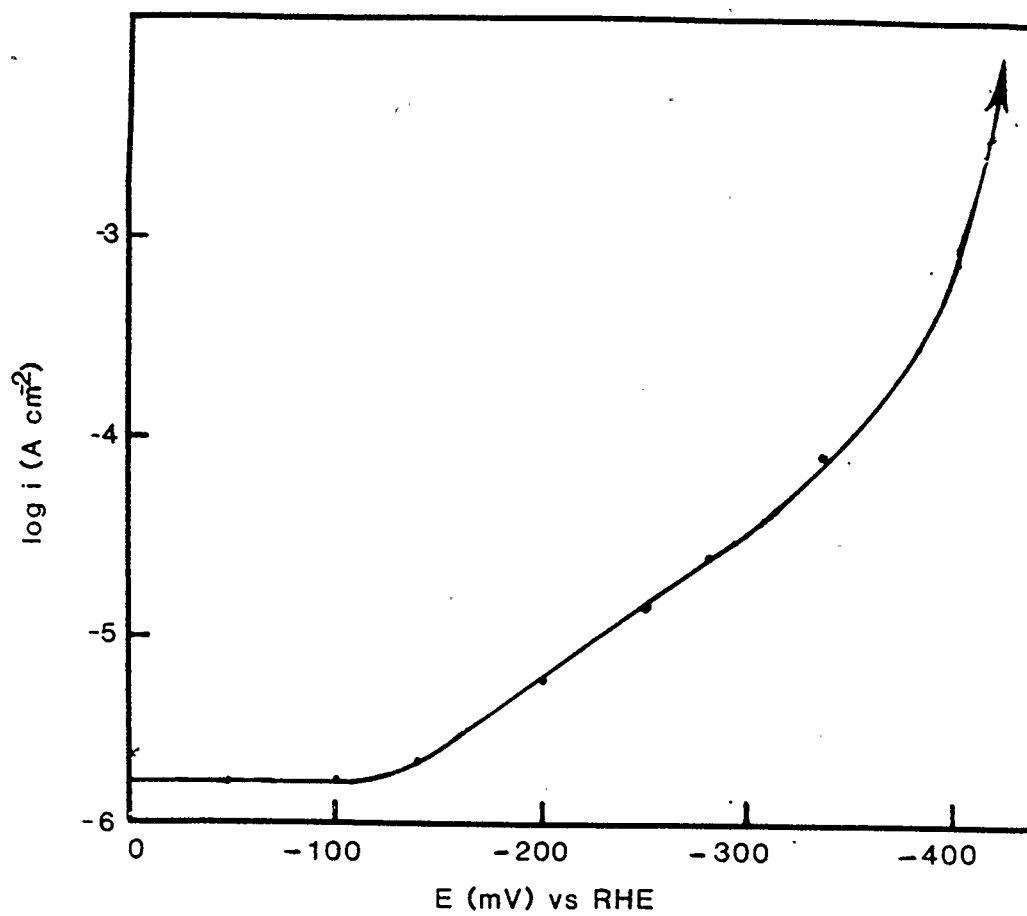


Fig. 6.8 Tafel plot for HER at oxidized alloy 1 (film thickness is ca. 700 Å).

obtained at any potential, and eventually, current densities greater than those at the "as-quenched" oxide-free surface were seen at the same potential.

The results at low overpotentials may indicate that the oxide layer initially serves as a barrier to the HER, permitting only a low rate diffusion controlled reaction, perhaps at pores in the film, to occur. This could be considered an advantage in terms of the corrosion resistance of these alloys, i.e. if hydrogen evolution is suppressed by the oxide.

Once the potential is extended to a critical value, the rate and mechanism of the HER become similar to those observed at the "as-quenched" alloy electrode, i.e. the oxide no longer serves as a barrier to the HER. This behavior can also be compared to the corrosion behavior of this oxidized glassy alloy (see section 6.5).

When the overpotential was greater than ca. -300 mV, the current density increased continuously with time at each potential. This indicates that, accompanying the HER, some oxide reduction may also be occurring (e.g. Ni(II) to Ni, Co(II) to Co). Fig. 6.9 shows a CV obtained after such an HER measurement. The reappearance of peak A₀ supports the suggestion of oxide reduction to metal.

A preliminary examination of the kinetics of the OER at this electrochemically oxidized glassy alloy electrode was also carried out in this work. Generally, Tafel slopes at

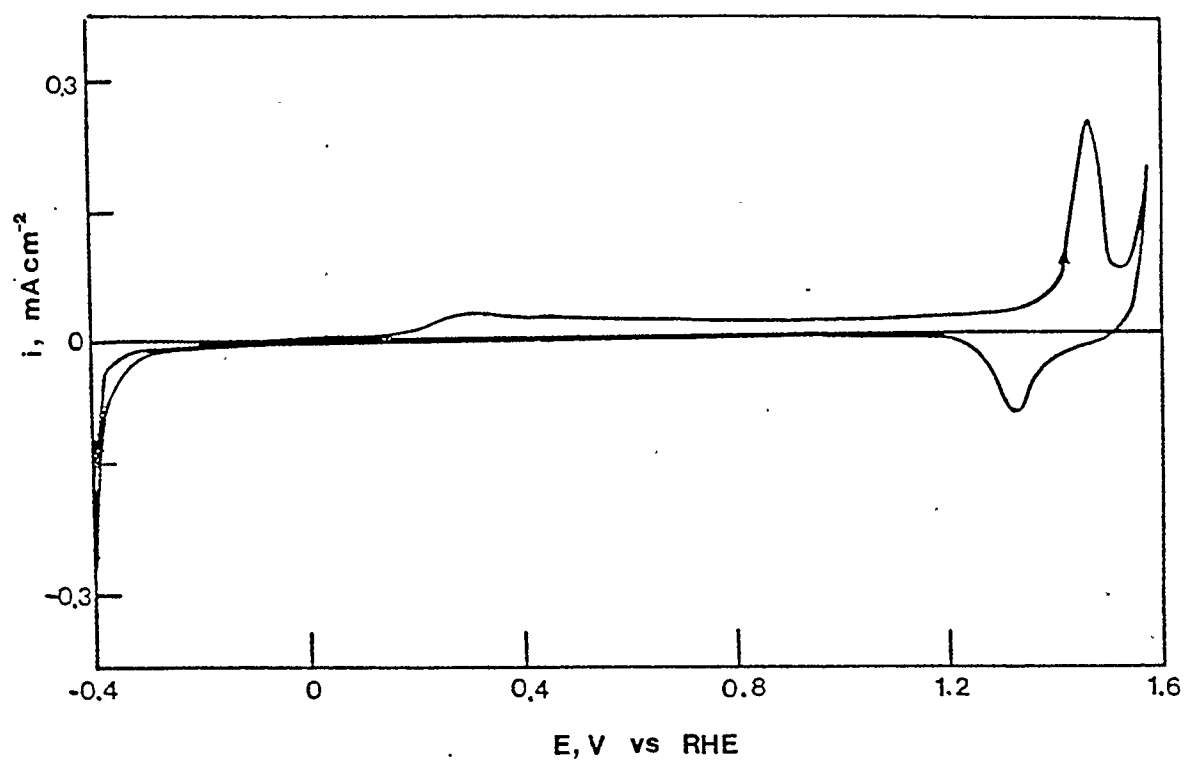


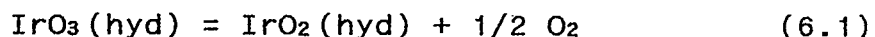
Fig. 6.9

CV for an oxidized electrode obtained after the
HER Tafel slope determination, $s = 100 \text{ mV/s}$.

oxidized electrodes have similar values (ca. 45 ± 5 mV/decade cd) to the oxide-free "as-quenched" glassy alloys.

A 40 mV Tafel slope has been reported for the OER at polycrystalline Ni [53], and NiCo_2O_4 [89] electrodes which have been subjected to potential scanning, while hydrous Co oxide electrodes have yielded a 52 mV/decade cd Tafel slope [71]. In the case of NiCo_2O_4 , it has been proposed [89] that a metastable NiCo_2O_4 spinel-type oxide forms. As discussed previously by Rasiyah and Tseung [101], the OER on the spinel NiCo_2O_4 may occur via the decomposition of a M(IV) oxide to M(II) oxide (M = Ni, Co), with the release of oxygen.

From the CV experiment, it is clear that the current of the OER is proportional to the magnitude of the A_2 and C_2 peaks (Fig. 6.1, curves a and b). This observation indicates that the OER might occur within the hydrous oxide. Similar suggestions have also been made by other authors for Ir [68]. At hydrous Ir oxide, decomposition of $\text{IrO}_3(\text{hyd})$ is thought to be involved in the OER reaction:



where 'hyd' represents hydrous oxide. This reaction implies that thicker hydrous oxide films could produce more oxygen, analogous to an electrode of higher surface area.

6.2 Oxide Growth Conditions for Alloy 1

Oxide growth at this glassy alloy was influenced by various factors, including $E(+)$, $E(-)$, s , etc. The results

of experiments carried out to test the relevance of these parameters are discussed below.

Positive Potential Limit ($E_{(+)}$)

The effect of $E_{(+)}$ on the oxide growth rate was studied by measuring the cathodic charge in peak C₂ after each potential scan. The relationship of oxide growth rate (i.e. the increase of charge density per cycle) vs. $E_{(+)}$ is shown in Fig. 6.10. It was found that the oxide growth rate increased with increasing $E_{(+)}$. This is similar to what has been reported for Ir hydrous oxide growth [83]. In the case of Ir, it was considered that the increase of $E_{(+)}$ leads to a more complete conversion of the underlying inner oxide layer to a hydrous oxide. It should be noted that when $E_{(+)}$ is more positive than 1.60 V, NiO₂ and CoO₂ can be formed [44,46,71], but they can rapidly decompose to Ni(II) and Ni(III), Co(II) and Co(III) oxides, thereby releasing oxygen, since they are very unstable.

As $E_{(+)}$ is made more positive, peak C₂ becomes somewhat asymmetrical, as a shoulder to peak C₂ appears at ca. 1.45 V (Fig. 6.1). This may be due to the reduction of some M(IV) oxide or of oxygen trapped in the oxide pores. The presence of this peak led to some difficulties in charge measurement and related calculations. Therefore, although the oxide growth rate is higher at more positive $E_{(+)}$, an $E_{(+)}$ of 1.55 V was generally used for thin oxides to minimize the OER, while an $E_{(+)}$ of 1.60 V was utilized with thick oxide films

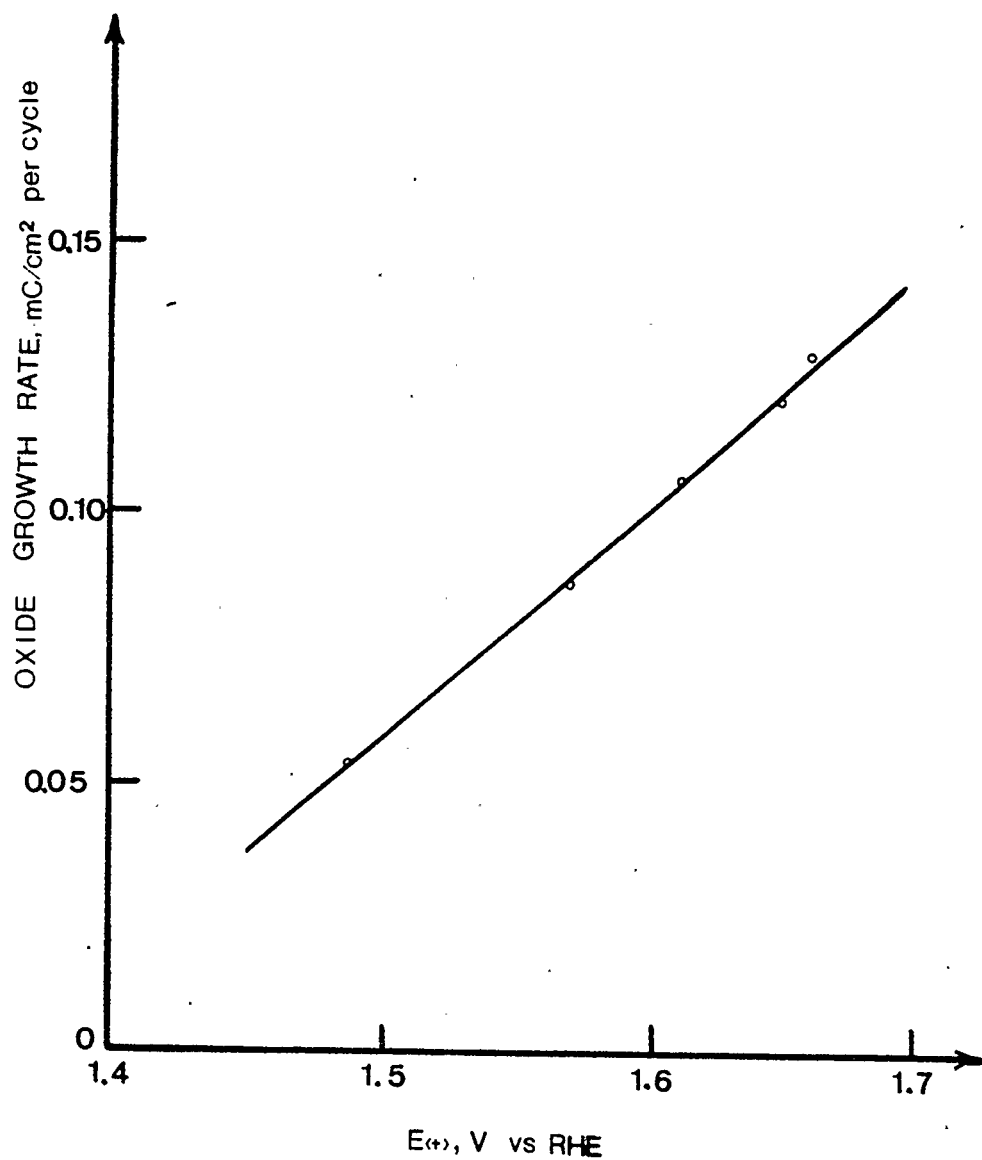


Fig. 6.10

The effect of $E(+)$ on oxide growth rate in 1 M NaOH (determined from peak C_2).

to overcome the increasing resistance of the oxide film.

Negative Potential Limit ($E_{(-)}$)

The influence of $E_{(-)}$ on the oxide growth rate is illustrated in Fig. 6.11. The charge density increases with a decrease of $E_{(-)}$ below 0 V, which is somewhat similar to Ir and Ni electrodes [47,69]. In the case of Ir [69], it is suggested that the potential must be extended sufficiently negatively in order to release the newly formed hydrous oxide from the underlying metal surface to the growing outer oxide. It is of interest that the oxide at this glassy alloy electrode continues to grow, although at a relatively low rate, even when $E_{(-)}$ is as positive as ca. 1.0 V. This observation is very different from that at polycrystalline Ni electrodes. In the case of Ni, no obvious charge increase is observed at $E_{(-)}$ more positive than ca. -0.25 V [47]. For example, at an $E_{(-)}$ of 0.98 V, no charge increase is seen after 72 minutes of potential cycling (Fig. 4.3), although the shapes of the oxidation and reduction peaks do change with time. At Ir electrodes, $E_{(-)}$ must be less than ca. 0.2 V for oxide growth to occur [69].

Potential Sweep Rate (s)

Fig. 6.12 demonstrates the effect of different potential sweep rates on the rate of oxide growth. The lower the sweep rate, the greater the charge increase per cycle, as more time is available per cycle. However, as more oxide can be grown per unit time at high s, for the purpose of experimental

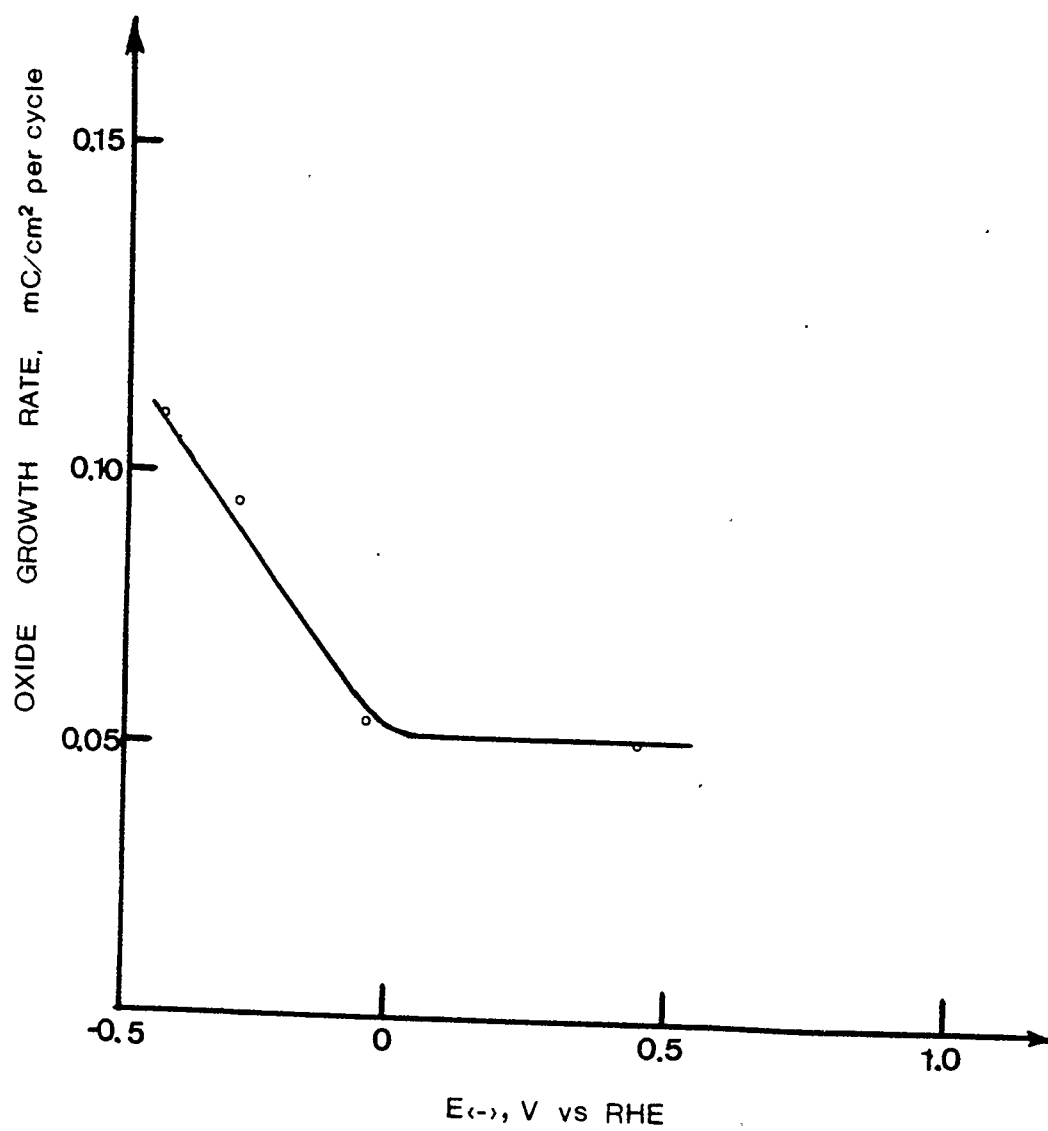


Fig. 6.11 The effect of $E(-)$ on oxide growth rate in 1 M NaOH (determined from peak C_2).

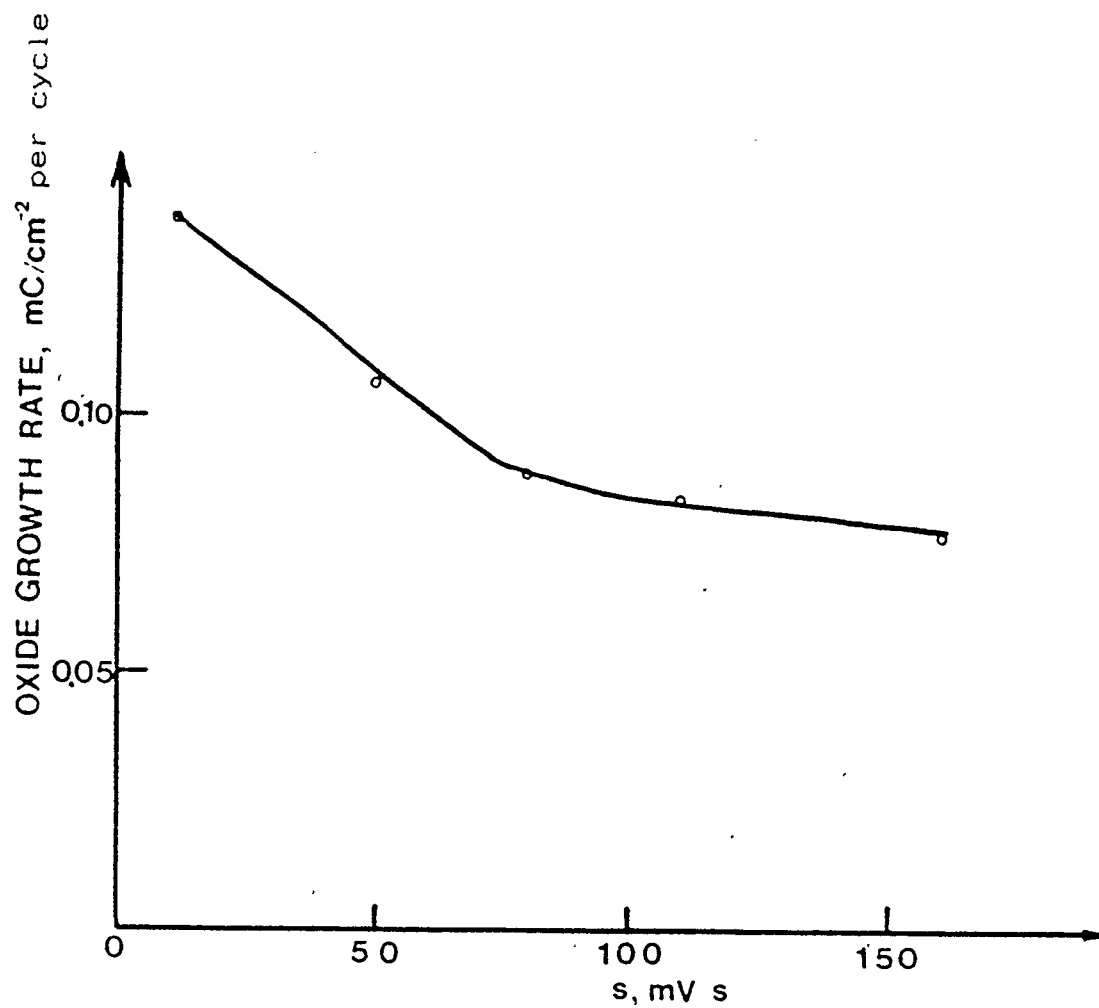


Fig. 6.12 The effect of potential sweep rate on oxide growth rate.

efficiency, a sweep rate of 100 mV/s was chosen for oxide growth in most of this work.

If the applied potential is changed from a triangular wave to a trapezoidal wave, the charge growth rate increased somewhat. Table 6-2 shows a comparison of the oxide growth rate as a function of $E(+)$ for those two methods. The maximum growth rate is obtained by the trapezoidal wave ca. 0.14 mC/cm² per cycle, as compared to 0.12 mC/cm² per cycle with the triangular wave. By examining Table 6.2, and comparing the magnitude of these charge densities with those obtained in the first and second potential scans at an "as-quenched" alloy electrode (Section 5.1), it is seen that these are quite similar.

These charge densities are also comparable to the single monolayer charge densities on Ir and Pt electrodes. In the case of Ir, a charge density of 0.11 mC/cm², corresponding to the "real" surface area, was obtained for one monolayer of Ir(III)/Ir(IV) oxide transformation [69]. At Pt electrodes, the charge density for one monolayer of PtO formation is ca. 0.44 mC/cm² [103].

In the present work, if it is assumed that the roughness factor is 1.5 to 2, the q of peak C_2 in the second potential scan is reasonably close to the q of one monolayer oxide. As the apparent electrode area was used, and as one monolayer of oxide is expected to be close to 0.10 to 0.11 mC/cm², the oxide growth rate of 0.14 mC/cm² per cycle is considered to

TABLE 6-2

OXIDE GROWTH RATE* UNDER VARIOUS
GROWTH CONDITIONS

<u>E(+)</u> (V vs. RHE)	<u>q (mC/cm²)**</u>	<u>q (mC/cm²)***</u>
1.49	0.05	0.07
1.57	0.09	0.11
1.65	0.12	0.14

* In 1 M NaOH, E(-) = -0.4 V, s = 100 mV/s.

** Without potential holding.

*** Potential was held at E(+), for 8 seconds.

be close to one monolayer of new hydrous oxide per cycle of potential. It appears that no more new oxide than this can be formed in a single cycle of potential, even under optimized conditions.

6.3 Potential-pH Dependence of Oxidized Alloy 1

After oxidation in 1 M NaOH solution for ca. 60 minutes, the electrode was transferred to solutions of various pH (from 12 to 14), but of identical ionic strength. Fig. 6.13 demonstrates a series of voltammograms obtained in this experiment. In this range of pH, the peak potentials of A₂ shifted negatively by ca. 85-95 mV (vs. SCE) and peak C₂ shifted ca. 70-80 mV with an increase of one pH unit. As the position and shape of the peaks were influenced by a number of factors such as film thickness, E(-) etc., the potential which is midway between peaks A₂ and C₂ (E_m) was used to track the E-pH relationship of the oxide reaction. This yielded a pH dependence of ca. 75-85 mV (vs. a pH-independent RE) per pH unit. This unusual E-pH relationship observed here is a very important indicator of the formation of a hydrous oxide [74,75,102].

The characteristics of hydrous oxides have been described in Chapters 2 and 4. The most important property of the hydrous oxides is their unusual 70 to 90 mV/pH dependence. The unusual ca. 90 mV/pH relationship can be expressed by the Nernst equation:

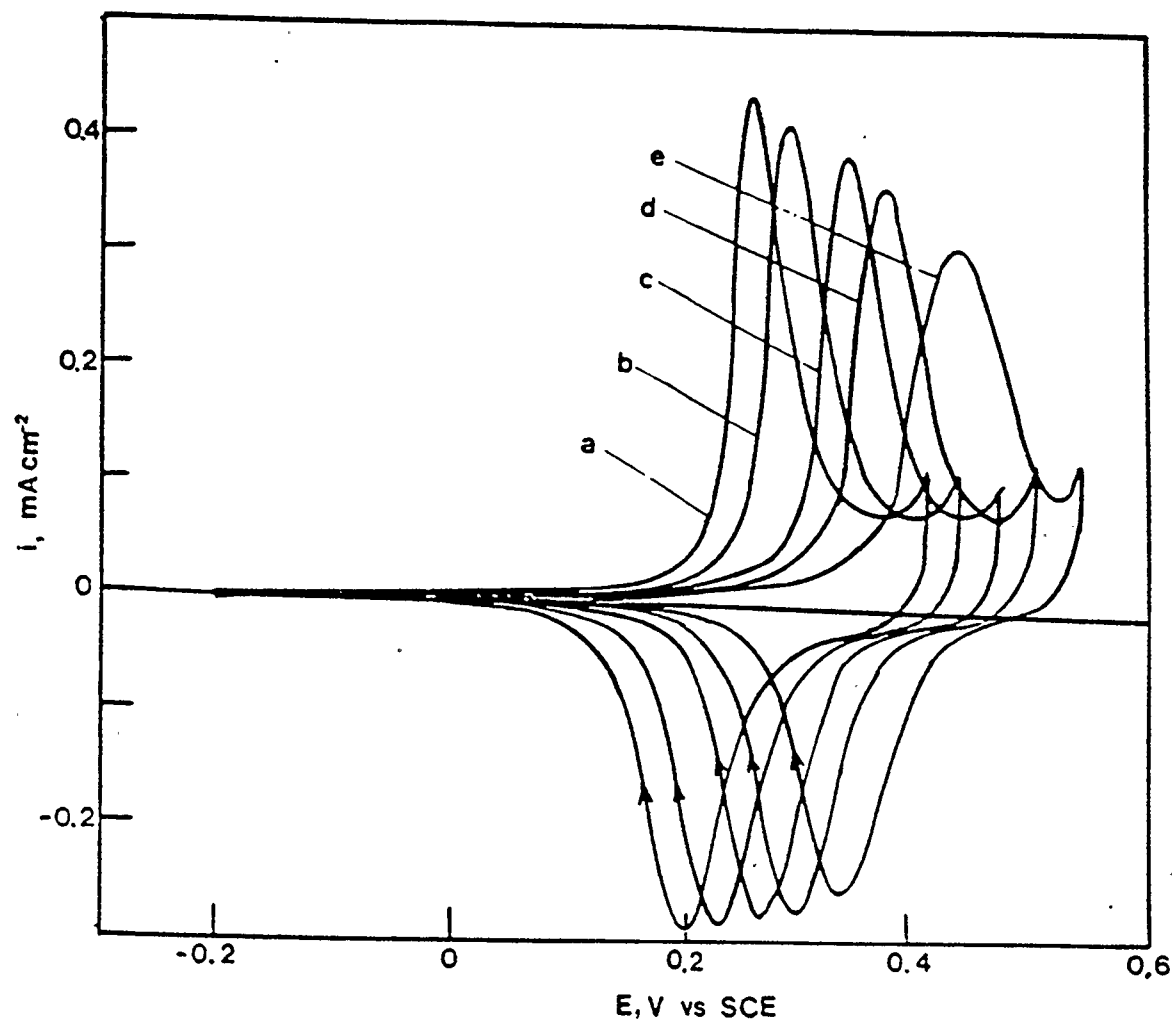
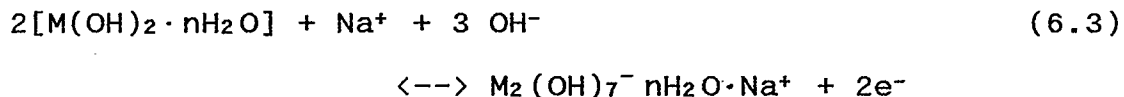


Fig. 6.13

CVs for oxide film on alloy 1, grown in 1 M NaOH for ca. 60 min, in solutions of varying pH. $s = 10 \text{ mV/s}$, pH of solution is (curve a) 14, (curve b) 13.5, (curve c) 13, (curve d) 12.5, (curve e) 12.

$$E^{0'} = E^0 - \frac{3}{2} \times 2.3 \frac{RT}{F} \times \text{pH} \quad (6.2)$$

In Equation (6.2), the ratio 3/2 must mean that, for each two electrons ejected during the oxidation, three OH⁻ ions are injected into (or three H⁺ are ejected out of) the oxide. This process leads the oxide being negatively charged. In order to maintain the charge balance inside the oxide film, counterions such as Na⁺ must enter the film. An electrochemical reaction which satisfies these facts can be written as [46]:



The XPS results, which have shown that Na is present in the oxide film in the oxidized state (Fig. 6.7), support this suggestion indirectly. This ion injection process may also bring a large amount of solvent into the film during its oxidation.

The electrochemical behavior of these films shows many similarities to some of the polymer modified electrodes [104-107]. In the case of these polymer electrodes, it is believed that during oxidation the film becomes swollen, being full of ions and solvent. During the reduction process, the film are thought to deswell, as ions and solvent are ejected from the films. Similarly, these hydrous oxides may also swell during oxidation. Upon reduction, the injection of two electrons will lead to the ejection of three OH⁻ ions from the film. Also, water and counterions will be

expelled. This could result in an increase in the compactness of the film and more cross-linking with oxygen and hydroxy species. A more detailed discussion of the analogies between these hydrous oxide films at glassy alloy electrodes and polymer-coated electrodes is presented in Chapter 7.

From the compositional and structural point of view, the formation of a hydrous oxide at this glassy alloy electrode is feasible, not only because both Ni and Co, in particular, have a tendency to form hydrous oxide films [46,71], but also because the noncrystalline nature of the alloy may favor the formation of amorphous oxide films. The 'mud-cracked' microstructure observed via SEM (Fig. 6.2) is further evidence supporting hydrous oxide formation at this alloy. The electrochromic behavior discussed above is also seen at metals which are known to form hydrous oxide films [47,66-71].

6.4 The Mechanism of Oxide Growth at Alloy 1 Electrode

The mechanism of hydrous oxide film formation has been studied by numerous researchers [69,108,109]. Generally, it is believed that the oxide film formed at Ir and Ni electrodes consists of an inner and an outer oxide. The inner oxide is thought to be anhydrous, compact and highly conductive, with a negligible potential drop across it. It is also believed to be only a few monolayers in thickness. In contrast, the outer oxide is believed to be hydrous,

porous and highly dispersed, and possibly very thick, depending on the experimental conditions [69]. The major potential drop is thought to be located across the outer surface of the compact film, i.e. at the inner and outer oxide interface [68,69].

Although there is no absolute evidence to prove the existence of an inner oxide at these glassy alloy electrode, by comparing the oxide growth characteristics and the general electrochemical behavior of this glassy alloy with that of Ir and Ni, one can see that it is reasonable to assume that the oxide formed at glassy alloy electrodes also consists of an anhydrous inner oxide and an outer hydrous oxide film. Therefore, by analogy with the suggested mechanism of hydrous oxide film formation at Ir electrodes [69], the mechanism of hydrous oxide growth at the Ni-based glassy alloy could be as follows.

At the start of the first anodic potential scan, some surface metal sites ($M = \text{Ni}$ and Co) are oxidized to $M(\text{II})$ oxide, e.g. $\text{Ni}(\text{OH})_2$ and $\text{Co}(\text{OH})_2$, at potentials of 0.3 to 0.4 V. The $M(\text{II})$ oxide/hydroxide film may be less than one monolayer in thickness, since at low potentials, the electrode surface also contains Cr and Mo. The surface-enriched Cr and Mo sites dissolve at potentials more positive than 1.0 V (peak A_1), thus allowing new Ni and Co sites to be oxidized to the $M(\text{II})$ state. At potentials near peak A_2 , the outer surface of the $M(\text{II})$ oxide can be oxidized to $M(\text{III})$

oxide. As the oxide tends to be negatively charged (reaction 6.3), counterions and water cause it to become hydrated. This attached hydrated M(III) oxide prohibits further oxidation of the inner layer because the hydrated layer forms a barrier between the inner layer and the solution.

During the cathodic potential scan, hydrous M(III) oxide is reduced to hydrous M(II) oxide in peak C₂. If the potential is scanned more negatively, some of the inner M(II) oxide is reduced to metal. At an E(-) of -0.4 V, the entire compact oxide can reduce. However, this E(-) is insufficiently negative to reduce the hydrous M(II) oxide to its metal state and therefore, it remains on the surface of the electrode.

During the next potential scan, the metal beneath the M(II) hydrous oxide is once again oxidized to form a compact M(II) inner oxide. Again, the outer surface of the inner oxide layer, together with the M(II) hydrous oxide, is oxidized to M(III). The new layer of oxide is again hydrated and the pattern discussed above is repeated in each cycle. The hydrous oxide accumulates on the electrode surface in this manner.

It has been pointed out that, under optimum conditions, the highest oxide growth rate is ca. 0.14 mC/cm² per cycle, which is very similar in magnitude to the charge density required for one monolayer of oxide to undergo a one electron oxidation/reduction reaction, as in the case of hydrous Ir

oxide films [69]. Assuming that 0.14 mC/cm^2 is equivalent to the charge density of one monolayer of hydrous Ni-Co oxide, the above model is supported. Fig. 6.14 is a possible schematic structure of this hydrous oxide film.

If the oxide growth rate is less than 0.14 mC/cm^2 (Fig. 6.11, Table 6-2), it is suggested either that only part of the inner oxide was oxidized at $E(+)$, or that not all of the inner compact oxide layer was reduced at $E(-)$, thereby failing to fully release the hydrous surface oxide to the bulk hydrous oxide.

6.5 Influence of Chloride on Oxidized Alloy 1 Electrode

The open circuit potential (OCP) of both the "as-quenched" and electrochemically oxidized glassy alloys was tested in borate buffered (pH 9.6) chloride solutions exposed to air. Table 6-3 gives OCPs of alloys having been subjected to different numbers of potential cycles in 1M NaOH, in comparison with Ni alone and "as-quenched" alloy 1. It can be seen that the "as-quenched" alloy has a much higher OCP than Ni, and the oxidized alloys have higher OCP than "as-quenched" alloy.

It is well known that the addition of Cr, or the combined addition of Cr and Mo, to glassy alloys is particularly effective in enhancing the corrosion resistance and passivating ability of many alloys [7,11-15,18]. However it is observed in Table 6-3 that the alloys which are more

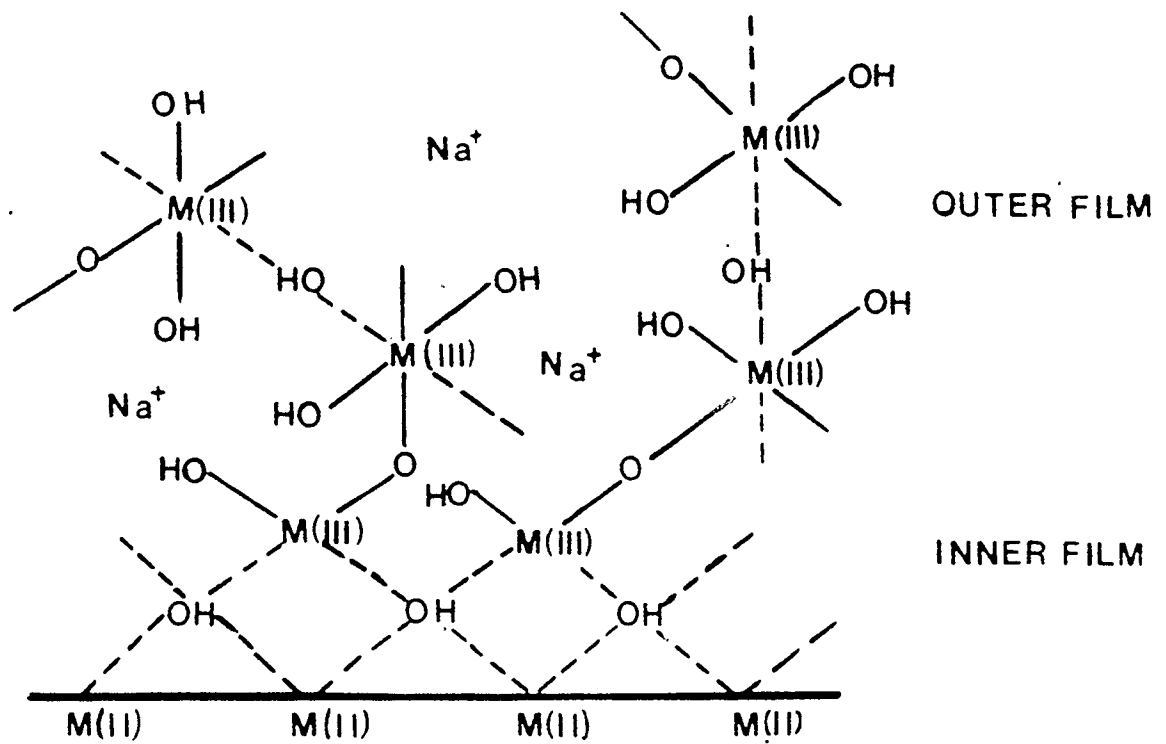


Fig. 6.14 Schematic model of the hydrous oxide film formed at alloy 1.

TABLE 6-3

OPEN CIRCUIT POTENTIAL OF THE OXIDE FILM IN
CHLORIDE CONTAINING SOLUTION

<u>ELECTRODE CONDITION</u>	<u>E (V) vs. SCE</u>
Ni	-0.55
"as-quenched"	-0.11
after 2nd scan	-0.03
550 Å	+0.17
1300 Å	+0.45
1600 Å	+0.52
6000 Å	+0.55

extensively oxidized display more positive OCPs than those with thinner oxide films. In the case of these oxidized hydrous Ni-Co oxides, very little Cr and Mo is present near the surface of the alloy due to their electrochemical dissolution. The results of Table 6-3 show that under open circuit conditions, an electrochemically formed hydrous oxide film appears to be a more effective barrier against chloride ions than is the enriched Cr/Mo region of the surface of an "as-quenched" alloy.

In order to further assess the susceptibility of this glassy alloy to oxidation in the presence of an aggressive ion such as chloride, slow sweep rate CV experiments were carried out in buffered neutral solutions, with and without added chloride. Fig. 6.15 (curve a) shows the i/E response of the "as-quenched" alloy in a borate-buffered (pH 9.6) 2×10^{-2} M chloride solution. Similar experiments were carried out with electrodes which had been oxidized to various extents in 1 M NaOH before transfer to the chloride-containing borate solutions. Fig. 6.15 (curve b) shows a CV obtained from an electrode covered with an oxide of ca. 1800 Å thickness oxide in the same solution. Both the "as-quenched" and oxidized electrodes exhibit a CV response which is characteristic of pitting. Also, some dissolved material could be seen near the electrode surface at positive potentials (Fig. 6.15) in both cases (curves a and b).

The CV of the oxidized alloy (Fig. 6.15, curve b) reveals

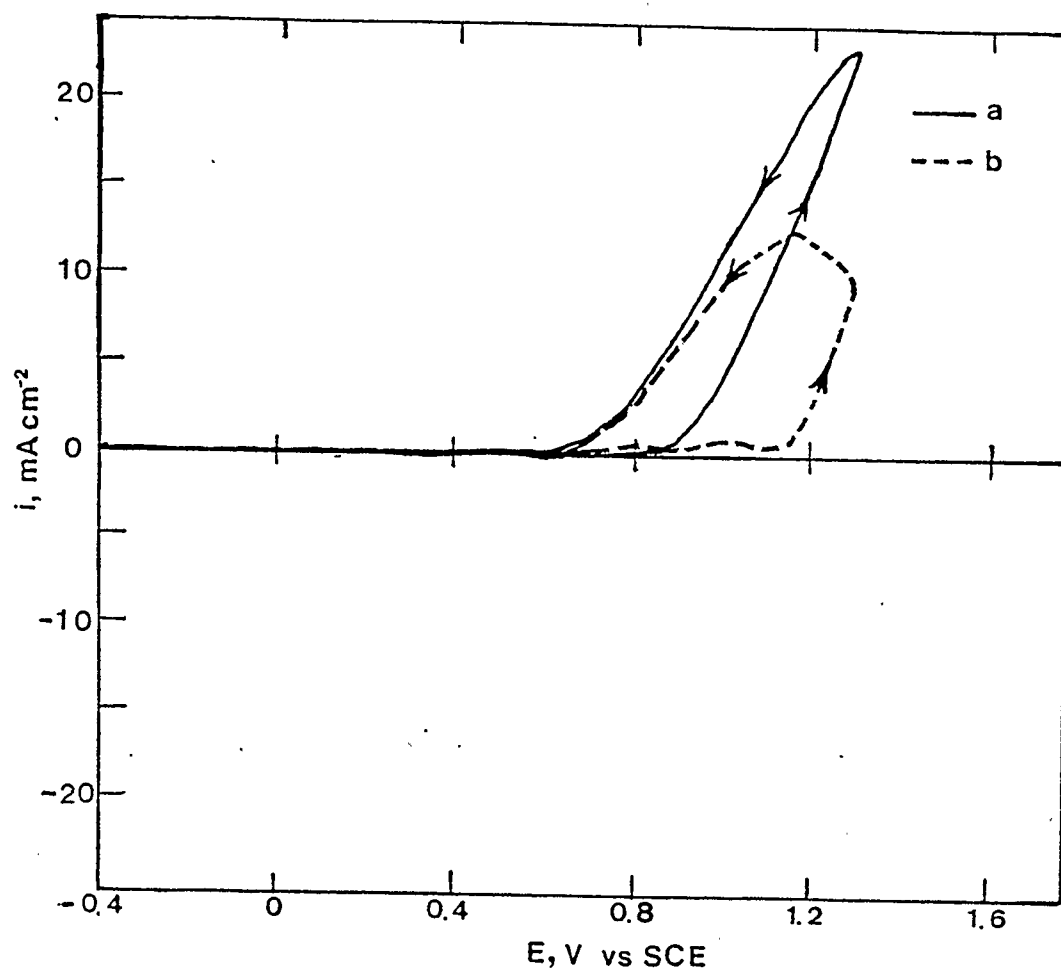
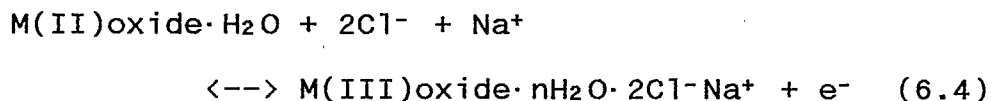


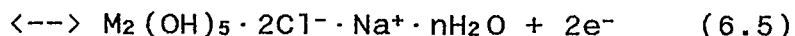
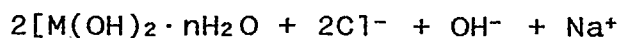
Fig. 6.15 CVs of "as-quenched" (curve a) and "oxidized" alloy 1 (curve b) in pH 9.6 solution with 2×10^{-2} M sodium chloride, $s = 2 \text{ mV/s}$.

first a small anodic peak, probably peak A₂, and then the rapid onset of an oxidation process at the "pitting potential" (E_p) which is about 300 mV more positive than in the case of the "as-quenched" electrode (curve a). However, in the negative scan for both electrodes, a similar "healing potential" (E_h) is observed for both electrodes. This may indicate that the electrochemically formed oxide film initially acts as a barrier to the chloride ion, but that as the potential is made more positive, the ion can penetrate the oxide, causing metal dissolution to occur.

The second positive-going sweep of the potential at an oxidized electrode in these chloride solutions shows a similar overpotential for pitting as in the first scan, indicating that chloride ions may have been expelled from the oxide during oxide reduction in the previous scan, and that it must be reinserted into the oxide in the next anodic sweep. The injection and expulsion of ions into and out of the oxide film is consistent with previously proposed mechanisms of charge transport in hydrous oxides and some modified polymer electrodes (see Section 6.1).

On the basis of these ideas, it is suggested that in the oxidation step in pH 9.6 chloride solutions, chloride ions are being drawn into the oxide film along with OH⁻, Na⁺ and water, e.g.





and vice versa in the cathodic step. This would explain the onset of pitting only after the film is oxidized.

It may also be important to recall that during the HER study, the oxide inhibited the HER initially; but once a critical negative overpotential was reached, it no longer served as a barrier to the reaction. This would be consistent with the ejection of OH^- (i.e. increasing acidity) from the oxide during reduction. This result is analogous to the situation in the presence of chloride ions at positive potentials and is indicative of the fact that ions and solvent are able to enter and leave the oxide as a function of potential, solution, etc.

6.6 The Electrochemical Behavior of oxidized Alloy 2

With continuous potential cycling, the magnitude of peak A_3 increased initially, then decreased and finally disappeared. Meanwhile, a new peak (A_3') at ca. 1.16 V, which is similar to the Co(II)/Co(III) oxide transition peak on Co CVs (Fig. 4.6), appeared and increased in magnitude with potential cycling (Fig. 6.16, curves a and b). Also, a peak which overlaps the OER appeared after several potential cycles. This peak is comparable to the Co(III)/Co(IV) oxidation peak. Now, the CV appears very similar to the CVs obtained on polycrystalline Co electrodes (Fig. 4.6),

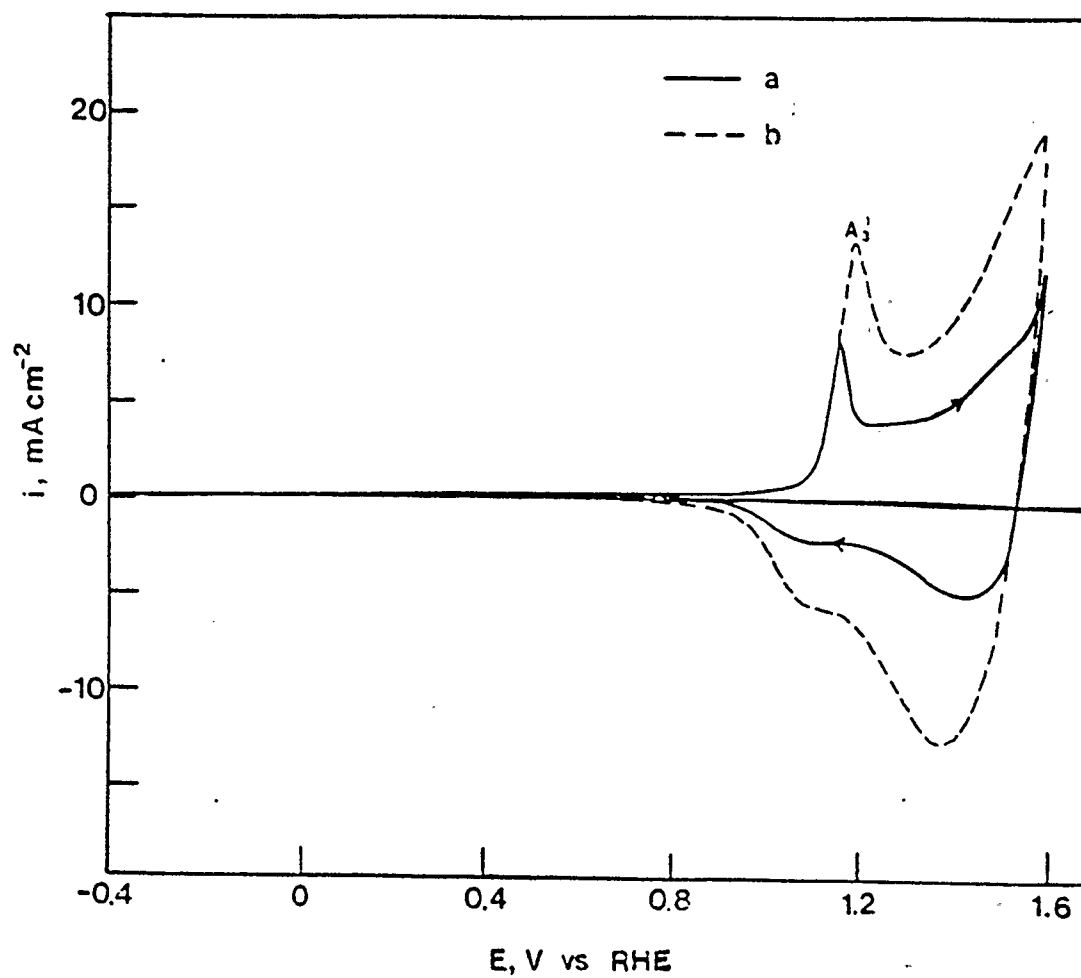


Fig. 6.16

CVs of an oxidized alloy 2, $s = 100 \text{ mV/s}$; (curve a) after 40 min. scan; (curve b) after 110 min. scan.

although no peaks are observed at negative potentials and very little HER current could be seen.

Overall, Figs. 5.9 and 6.16 can be explained in the following way: at the "as-quenched" glassy alloy 2, Cr is highly enriched on the surface but it dissolves with potential cycling. Since the Cr content of alloy 2 is quite high (ca. wt 27%), the complete electrodisolution of Cr requires several potential scans. The first CV (Fig. 5.9, curve a) appears to be dominated by Cr electrochemically. With the loss of Cr from the surface, more Co is exposed to the solution, and the CV response becomes more similar to the CV obtained for Co (Fig. 6.16, curves a and b).

The oxide on Co-based glassy alloys is also found to grow with continuous potential cycling, although it does not grow as rapidly as the oxide at the Ni-based alloy (alloy 1). During the potential cycling, very obvious electrochromic behavior, together with interference color changes were seen. The electromicrograph of this film is shown in Fig. 6.17. The film appears to be very smooth, which is quite different from the oxide formed at Co electrodes (Fig. 4.7). Two layers were seen on the substrate. No detailed research has been done, but it would be a significant result for the study of hydrous oxide formations on this alloy. Further studies are expected in the future.

Overall, it can be concluded from the discussion in this chapter that a hydrous oxide film can be formed electro-

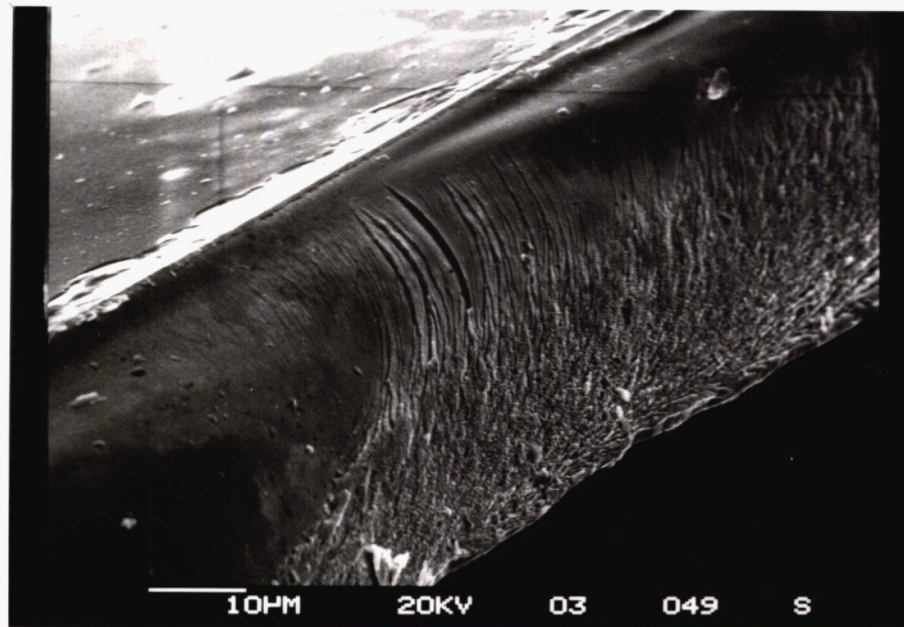


Fig. 6.17 SEM photograph of oxidized alloy 2; the potential was scanned for ca. 110 min. in 1 M NaOH.

chemically at the surface of alloy 1. The hydrous oxide film possesses special characteristics which are similar to those of Ir, Ni and other hydrous oxides. The mechanism of the oxide growth is considered to be analogous to that of Ir hydrous oxide film.

Chapter 7

THE KINETICS OF OXIDATION/REDUCTION OF HYDROUS OXIDE
FILMS AT GLASSY ALLOY ELECTRODES

The kinetics of oxidation and reduction of electrochemically generated hydrous oxides at these Ni-based glassy alloys has been studied, in order to compare them with those of hydrous Ir oxide [102,111] and polymer modified electrodes [104-108]. In addition to cyclic voltammetry, chronoamperometry was also utilized in this study, since it can provide detailed information of complex electrode reactions and kinetics. Also, since the IR drop can be minimized in chronoamperometry, it is a very good supplement to the CV experiments. The results of these experiments are discussed below.

7.1 Cyclic Voltammetric Behavior

Fig. 7.1 shows that, for a thin hydrous oxide film (ca. 500 Å), the cathodic peak current (I_{cp}) is linearly proportional to s . However, the situation is different for a thick oxide film (ca. 3600 Å). In Fig. 7.2 (curve a), it can be seen that the linear I_{cp} - s relationship is obtained only at low sweep rates. At higher sweep rates, a linear I_{cp} - $s^{1/2}$ relationship is obtained (Fig. 7.2, curve b).

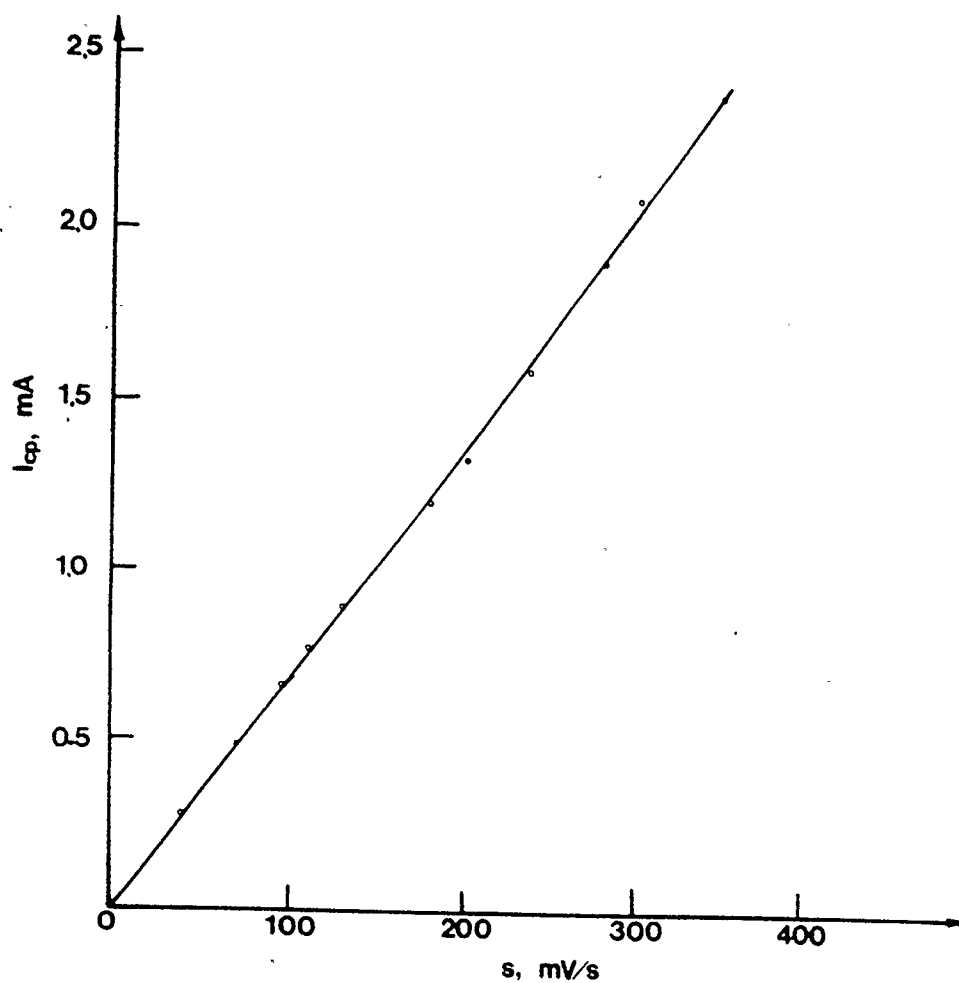


Fig.7.1

The peak current of oxide reduction versus potential sweep rate (thin oxide film, ca. 500 Å); $E(-) = 1.14 \text{ V}$, $E(+) = 1.56 \text{ V}$. The potential was scanned forward at 100 mV/s, and held at $E(+)$ for ca. 10 sec.

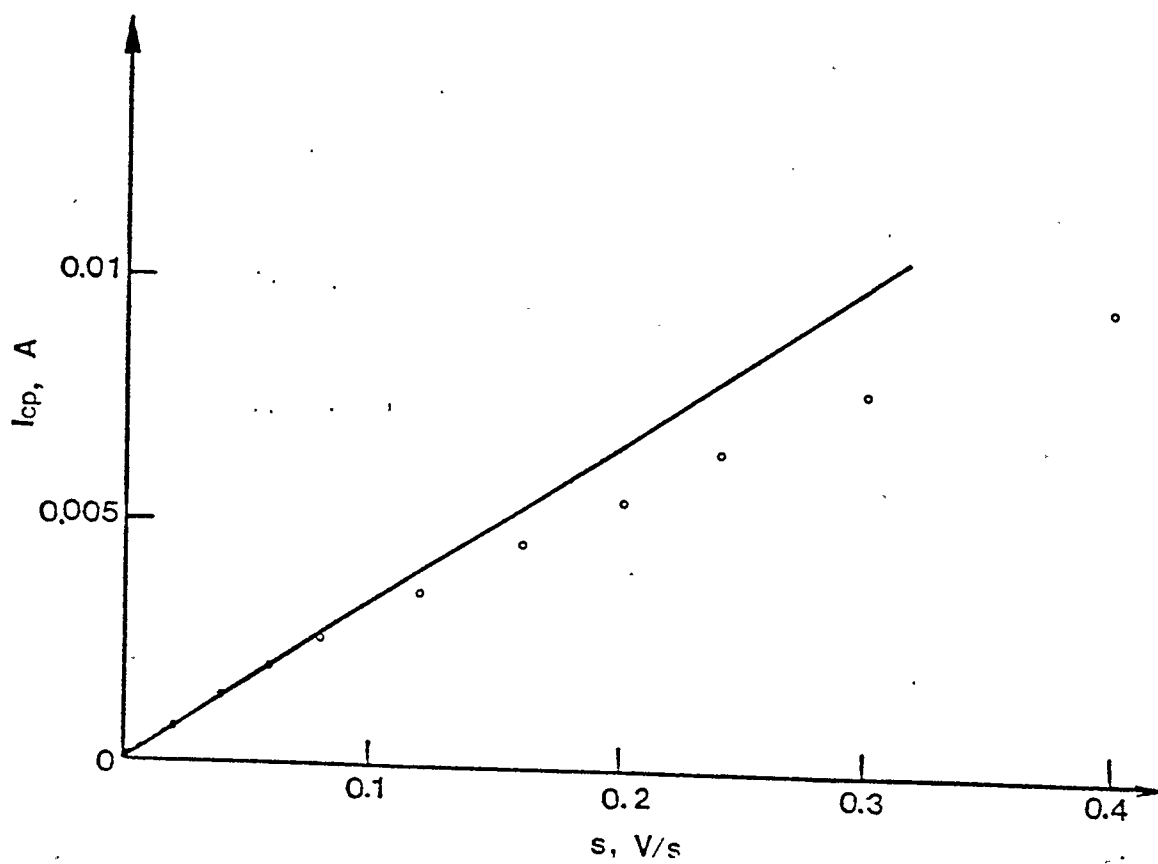


Fig. 7.2 (a) The cathodic peak current of oxide reduction versus potential sweep rate (the oxide film thickness is ca. 3600 Å).

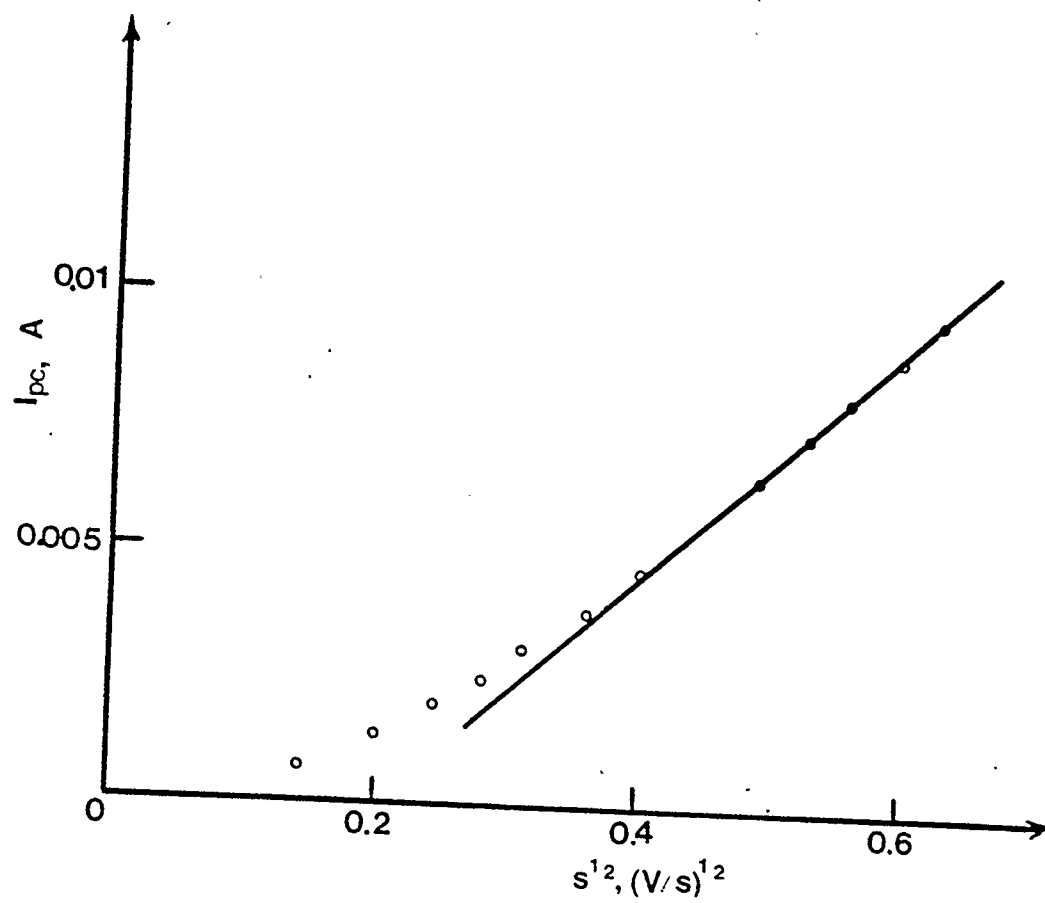


Fig. 7.2 (b) The cathodic peak current of oxide reduction vs. square root of sweep rate (I_{cp} vs. $s^{1/2}$).

Some similarities of these results to those obtained with polymer-coated electrodes, where the oxidation and reduction reactions are thought to occur via electron transfer (hopping) between the electroactive centers, have been found. Associated with the electron hopping process, the transport of charge compensating counterions from the solution into/out of the films, as well as solvent flow and polymer chain motions, are thought to occur [104-108]. All of these processes together are referred to as the "charge transport" process in much of the polymer literature [104,105].

If the rate of charge transport through these polymer films is fast enough so that the film oxidation/reduction processes obey the Nernst equation at each potential, a linear I_{cp} - s relationship is obtained [105]. If the oxidation/reduction process is limited by diffusion of counterions within the film, a linear I_{cp} - $s^{1/2}$ relationship is expected. If electron hopping is the rate determining step, this has been shown to be mathematically equivalent to diffusion [104,105,109,110] and a linear I_{cp} - $s^{1/2}$ relationship should also be observed.

This argument can also be applied to the hydrous oxide film formed on alloy 1 (Figs. 7.1 and 7.2). At an electrode covered with a thin oxide film, electron hopping between the electroactive centers, as well as counterions and solvent motion, appear to be rapid, as a linear I_{cp} - s dependence is observed. However, in the case of a thick oxide film, when a

linear $I_{cp}-s^{1/2}$ relationship is obtained (Fig. 7.2 curve b), either electron hopping or ion diffusion may be rate limiting.

The semi-infinite linear diffusion equation, showing a linear $I-s^{1/2}$ relationship, can yield the diffusion coefficient (D)

$$I_p = (2.69 \times 10^5) n^{3/2} A D_{app}^{1/2} s^{1/2} C \quad (7.1)$$

where D_{app} is composed of the contribution of ion diffusion and electron hopping within the film. An attempt was made to estimate D_{app} from the slope of the plot in Fig. 7.2 (curve b). In equation (7.1), s is sweep rate in V/s, A is electrode area in cm^2 , and n is assumed to be 1. C is the concentration of electroactive sites within the film in mol/cm^3 . The concentration C is not known, but can be obtained from indirect methods [111]. According to Faraday's law,

$$C = Q/nFV \quad (7.2)$$

where F is the Faraday constant and V is the volume of the oxide in cm^3 , and can also be written as $A \times d$. The parameter d is the thickness of the oxide film in $\text{\AA}$, which can be obtained from SEM analyses (Fig. 6.5). Therefore, equation (7.1) can be re-written as

$$I_{cp} = 2.79 n^{1/2} Q D^{1/2} s^{1/2} / d \quad (7.3)$$

If the slope of the $I_{cp}-s^{1/2}$ plot is $0.022 \text{ As}^{1/2}/V^{1/2}$, Q obtained from CV is $5.5 \times 10^{-3} \text{ C}$, and the thickness of the film is ca. $3600 \text{ \AA}$, then D_{app} is estimated to be ca. $2.6 \times$

10^{-9} cm²/s. Here, the main sources of error are in charge measurement, the estimation of film thickness, the assumption that $n = 1$, etc., which errors are difficult to estimate, but likely to be large. This D_{app} value will be compared with those D_{app} obtained from i/t determinations below, and with those D_{app} at Ir hydrous oxide and polymer modified electrodes.

The shape and position of peak A₂ are found to depend greatly upon the negative limit of the potential scan. For example, when $E(-)$ is 1.0 V (Fig. 7.3, curve a), peak A₂ is quite broad, symmetrical and similar in shape to peak C₂. Peak A₂ is shifted positively and becomes asymmetrical at $E(-) = 0.0$ V (curve b), although the charges in peaks A₂ and C₂ remain equivalent.

It has also been reported that, at polymer-coated electrodes, the peak potential depends upon many factors, including sweep rate, potential limits and the delay time between successive sweeps [105,107,108]. This was explained in terms of variations of the film resistance. It is known that ions and solvent are drawn into the polymer film during its oxidation. Therefore, a fully oxidized and swollen film is considered to be like a 'concentrated solution', with a very low resistance [104,107,108]. The film becomes de-swollen and compact after reduction, as counterions and solvent are ejected. As the film now has a low internal electrolyte concentration, its resistance increases.

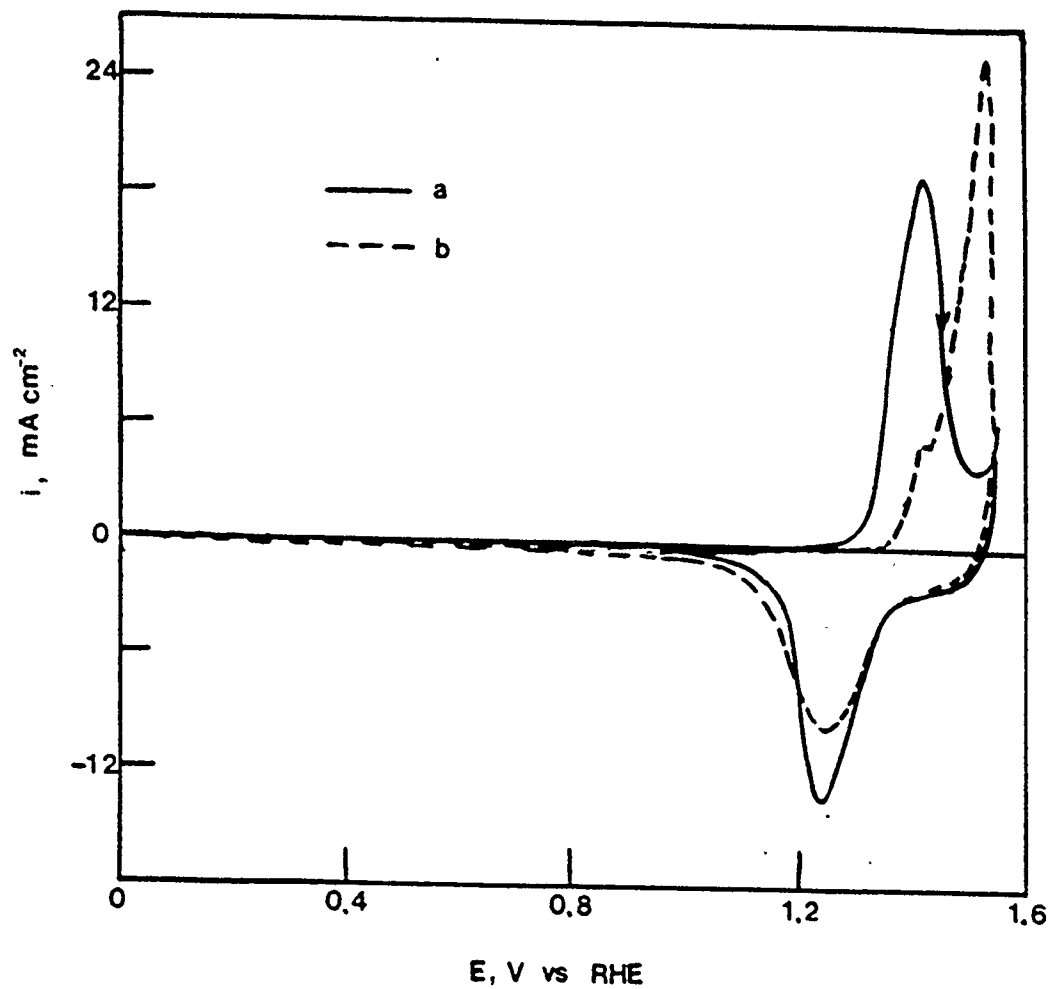


Fig. 7.3

CVs for an oxide film at different $E(-)$; $s = 100$ mV/s ; (curve a) $E(-) = 0.98$ V; (curve b) $E(-) = 0$ V.

In Chapter 6 of the present work, it has been suggested that the transport of ions and solvent accompany the Ni/Co oxide film oxidation and reduction reactions. It is also possible that the film becomes more resistive during reduction and less resistive during oxidation. The more negative the $E_{(-)}$, the more completely ions and solvent are expelled (i.e., the film becomes more compact and more highly cross-linked), hence the higher the film resistance.

If $E_{(-)}$ is not negative enough to reduce all of the sites, and thus not all of the ions and solvent are expelled from the oxide film during the reduction process. The film may then remain somewhat swollen, open in structure and with little resistance. Therefore, peak A_2 remains broad, and peaks A_2 and C_2 appear to be more reversible. Since the oxidized film is full of OH^- and Na^+ ions, as well as H_2O , its resistance is relatively low and, therefore, the cathodic peak always remains relatively broad in shape.

It is also observed (Figs. 6.1 and 7.1) that the anodic peak (A_2) is much sharper and narrower (peak-width-at-half-height, $\Delta E_{1/2}$, of ca. 50–80 mV), than its cathodic counterpart, ($\Delta E_{1/2}$ of ca. 85–120 mV). These values are not in agreement with the theoretical value of 90 mV for a one electron transfer surface reaction (without lateral interactions) [105,112].

The CV peak shapes obtained from oxidized glassy alloy electrodes (e.g., Fig. 6.1 and 7.1) can be explained in terms

of the presence of attractive and repulsive interactions between the electroactive sites within the oxide film. According to Conway et al., $\Delta E_{1/2}$ is an almost linear function of the interaction parameter, g [112]. Positive g values represent repulsive interactions, and negative g values imply attractive interactions between sites within the film. It has also been suggested, by Bard et al. [105], that attractive interactions between oxidized centers within the film enhance the rate of oxidation and result in sharp and narrow peaks (A_2). Repulsive interactions have the opposite effect, and broaden the CV peaks.

Based on the observed 90 mV/pH dependence of peaks A_2 and C_2 , and the results obtained with Ni and Ir hydrous oxide film [46,73,102], the oxidized sites in the film can be considered to have excess OH^- ions at the metal ion sites (with Na^+ counterions in solution in pores of the film), e.g. $M_2(OH)_7^- \cdot Na^+$. Therefore, repulsive interactions may occur between the OH^- species attached to the oxidized centers, causing a broad reduction peak. The narrow and sharp anodic peak may reflect the presence of attractive interactions between the electroactive centers after the film reduction. This is consistent with the suggestion that reduced films are more compact and cross-linked, while oxidized films are swollen.

Further evidence for the effect of attractive and repulsive interactions within films comes from research with

polymer modified electrodes. Pearce and Bard [105,110] also discussed the shape of CV peaks in terms of lateral interactions, a concept similar to that of Conway [112]. According to Pearce and Bard, attractive interactions ($g < 0$) between the oxidized centers yield oxidation and reduction peaks which shift negatively. However, in this work, although the anodic peak is narrow and sharp, it has been observed to shift to more positive potentials with more negative $E(-)$ and increasing film thickness.

There are other possible interpretations of the shape of peaks A_2 and C_2 in this work. These could include the variation of the activity of oxidized sites in the film with potential, since the film is known to swell and deswell during oxidation and reduction, respectively [106]. Also, since the oxide film is a mixture of Ni and Co oxides with unknown distribution, different areas of the film may have different average E^0 's. This overlapping range of E^0 's may lead to broad peaks [113]. But, this does not explain the narrow anodic peak (A_2) in the present work.

It can also be seen in Figs. 6.1 and 7.1 that, if $E(-)$ is less than 0.0 V, a small shoulder on the negative side of peak A_2 is observed at ca. 1.37 V. This shoulder appears only when the oxide film exceeds a thickness of ca. 1500 Å, at which point the potential of A_2 shifts positively. This shoulder may be due to the oxidation of the inner oxide, if this amorphous alloy behaves like Ni electrodes (Section

4.1); or it may be due to a "break-in" effect, which has been discussed by Murray et al. in terms of polyvinyl-ferrocene coated electrodes [104]. Since the resistance of the film is high after reduction, film 'break in' is considered to occur only at a few sites initially (shoulder). As counterions and solvent are drawn in, the film swells, the film resistance is lowered and hence the entire oxide becomes active (peak A₂). It is not clear, at this stage, whether this shoulder is inherent to this glassy alloy, or is an artifact caused by film resistance during the film 'break-in' process. Further study and quantitative interpretation of this shoulder is expected in the future.

7.2 Chronoamperometric Behavior

Fig. 7.4 shows typical chronoamperometric responses of a thin oxide film (ca. 120 Å) subjected to a square wave potential program from 1.0 V to various E₍₊₎ values. At an E₍₊₎ of 1.35 V, a normal current decay to zero was observed (Fig. 7.4, curve a). At an E₍₊₎ of 1.38 V (Fig. 7.4, curve b), the i/t curve exhibits an abnormal current maximum before decaying to zero. This current peak becomes sharper and occurs at shorter times with increasing E₍₊₎ and is no longer visible when E₍₊₎ reaches ca. 1.45 V (Fig. 7.4, curves c and d). The cathodic i/t response demonstrates an exponential decay to zero at all E₍₊₎. The cathodic currents are proportional to t^{-1/2} (Fig. 7.5), indicative of a diffusion

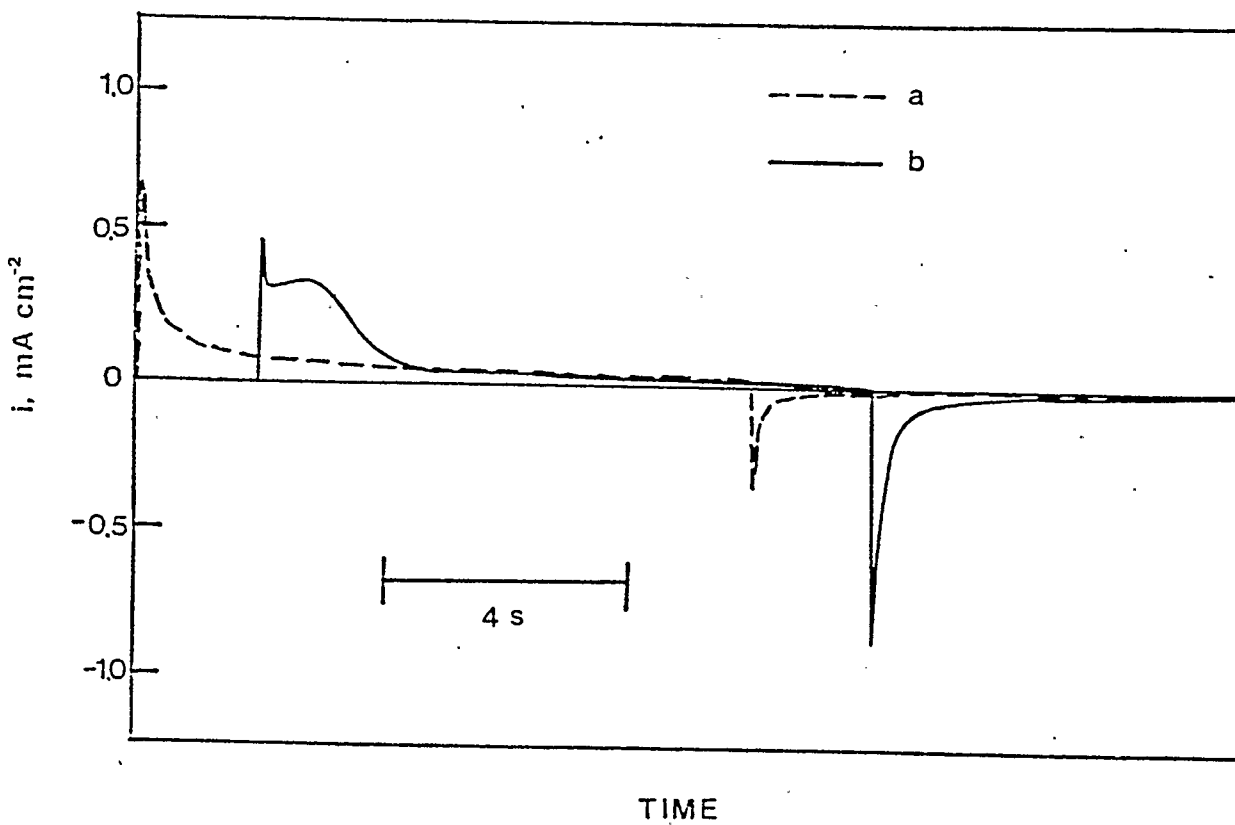


Fig. 7.4a

The i vs. t responses to various $E(+)$ for oxide film of ca. 120 Å thickness, $E(-) = 1.0$ V; (curve a) $E(+)$ = 1.35 V; (curve b) $E(+)$ = 1.38 V.

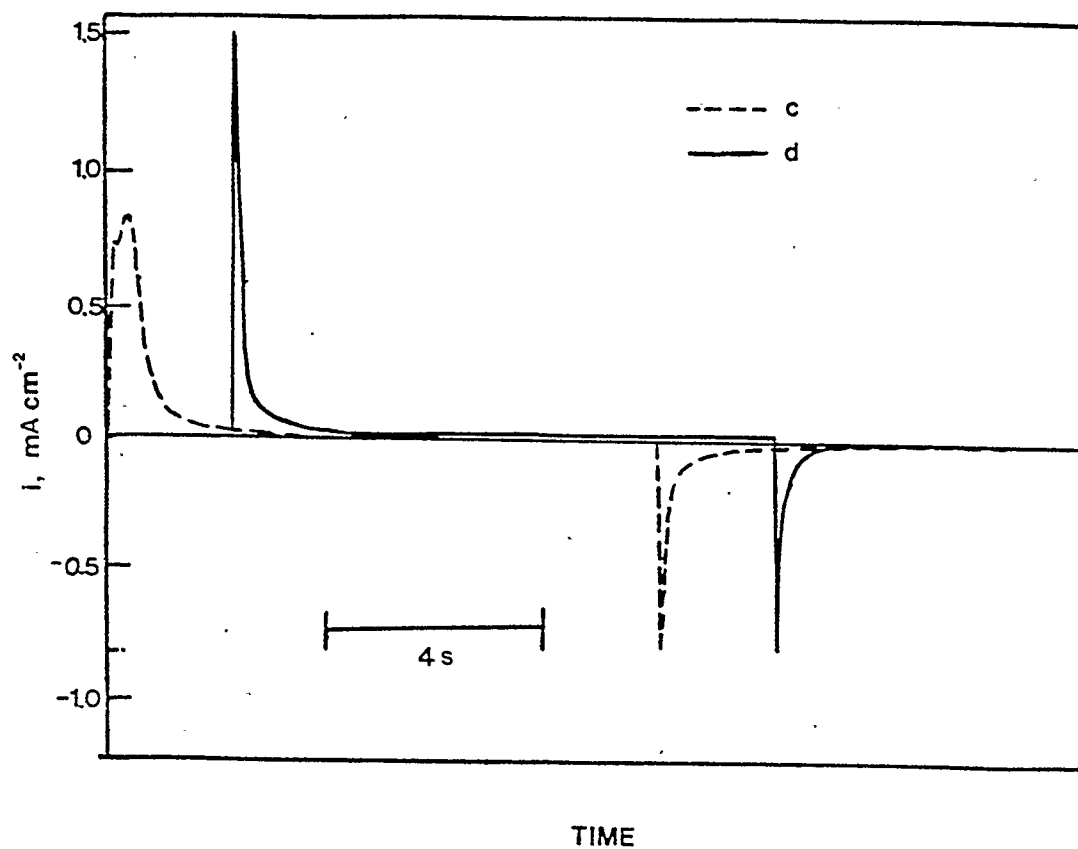


Fig. 7.4b

The i vs. t responses to various $E_{(+)}$ for oxide film of ca. 120 Å thickness, $E_{(-)} = 1.0$ V; (curve c) $E_{(+)} = 1.40$ V; and (curve d) $E_{(+)} = 1.45$ V.

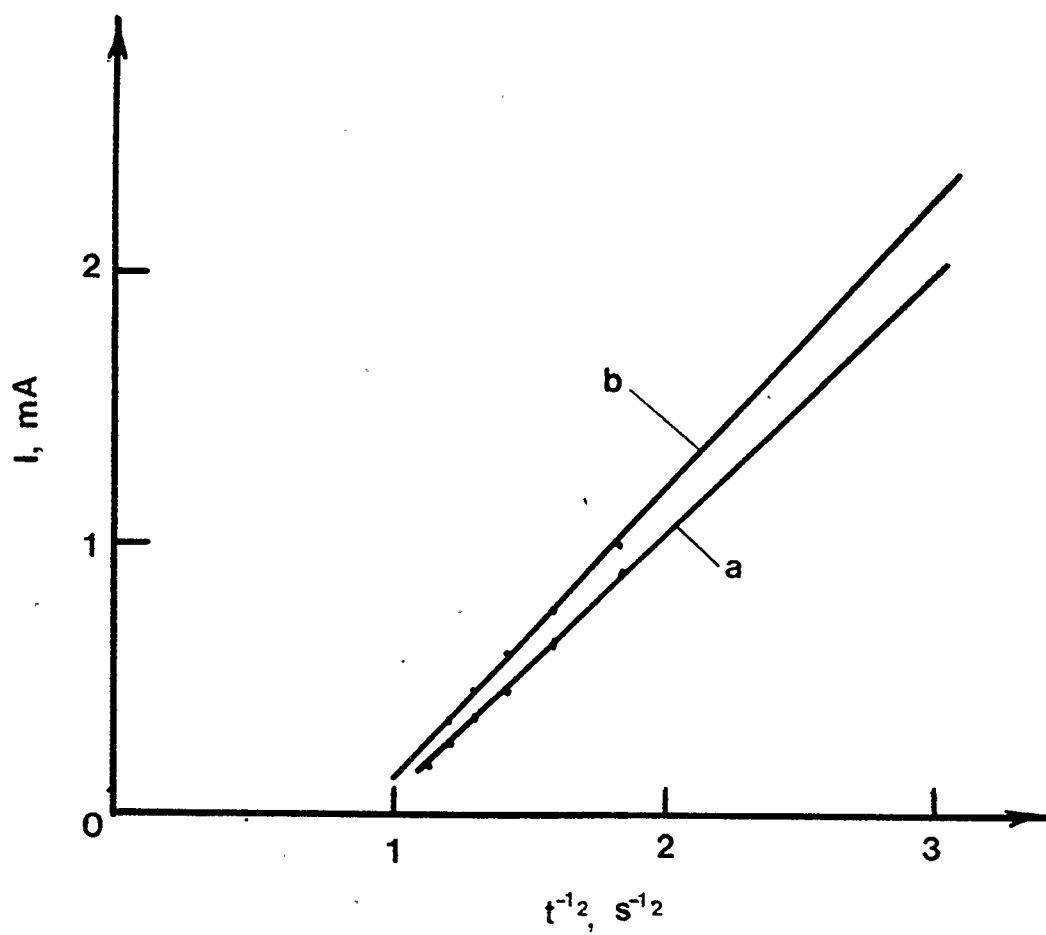


Fig. 7.5

Cottrell plots (I vs. $t^{-1/2}$); (curve a), $E_{(+)} = 1.45 \text{ V}$; (curve b) $E_{(+)} = 1.50 \text{ V}$.

controlled process [105]. It is also noted that the charge passed during the anodic process is greater than that of the cathodic process over a particular $E(+)$ range. This will be discussed in Section 7.3.

A similar sequence of anodic i/t response as a function of $E(-)$ was also observed with Ni electrodes by Pickett and Malay [82]. However, if 10 % of Co was co-precipitated on the Ni electrode, the anodic current peak disappeared. In the present work, the maximum in the anodic i/t response was not observed with Ni, Co or Ni-Co co-precipitated electrodes.

Once again, results similar to Fig. 7.4 have been reported by numerous researchers for polymer modified electrodes [104,107,108]. In those studies, a peak in the anodic i/t response was considered to be related to the "film ohmic resistance", a potential-dependent resistance to ion and solvent flow within the polymer film. If $E(+)$ is not positive enough to overcome this resistance, the film cannot be rapidly activated initially. A certain amount of time and a critical internal concentration of ions and solvent is required to "break-in" the film, causing the resistance drop [104,108]. In contrast, the cathodic i/t response does not show a peak, as the film is full of ions and solvent in the oxidized state so that the film resistance is low.

Normally, a current maximum in an i/t response can imply that a nucleation process has taken place [114,115]. In the present case, the current peak in the i/t response may be

connected with both a type of nucleation process and film resistance. During the film "break-in" process, only a few sites in the film are oxidized, causing some ions and solvent to enter the film. This could then "catalyze" the oxidation of the entire film. Although this is also related to film resistance, it could lead to a nucleation-like i/t response.

The shape of the i/t curves for these oxidized glassy alloy electrodes are also found to depend greatly on both $E_{(-)}$ and on the pulse width. Fig. 7.6 demonstrates the influence of $E_{(-)}$ on the anodic i/t response. It is obvious that the more negative the $E_{(-)}$, the more likely it is that an i/t peak will be observed. This is consistent with the results obtained from the CV experiments, in which a more negative $E_{(-)}$ caused peak A_2 to shift positively and become narrower.

In the i/t transient experiment, if the $E_{(-)}$ was as high as ca. 1.24 V, a smooth anodic current decay was obtained, even at $E_{(+)}$ = 1.37 V, at which the abnormal current maximum is usually seen. The absence of the peak when $E_{(-)}$ = 1.24 V may be related to the fact that as the film is not fully reduced at this $E_{(-)}$, not all of the ions and solvent are expelled from the film and therefore, the film remains relatively conductive.

The influence of the potential pulse width (time at $E_{(+)}$ and $E_{(-)}$) on the i/t response was also investigated. It has been found that the current at the maximum was lower and the

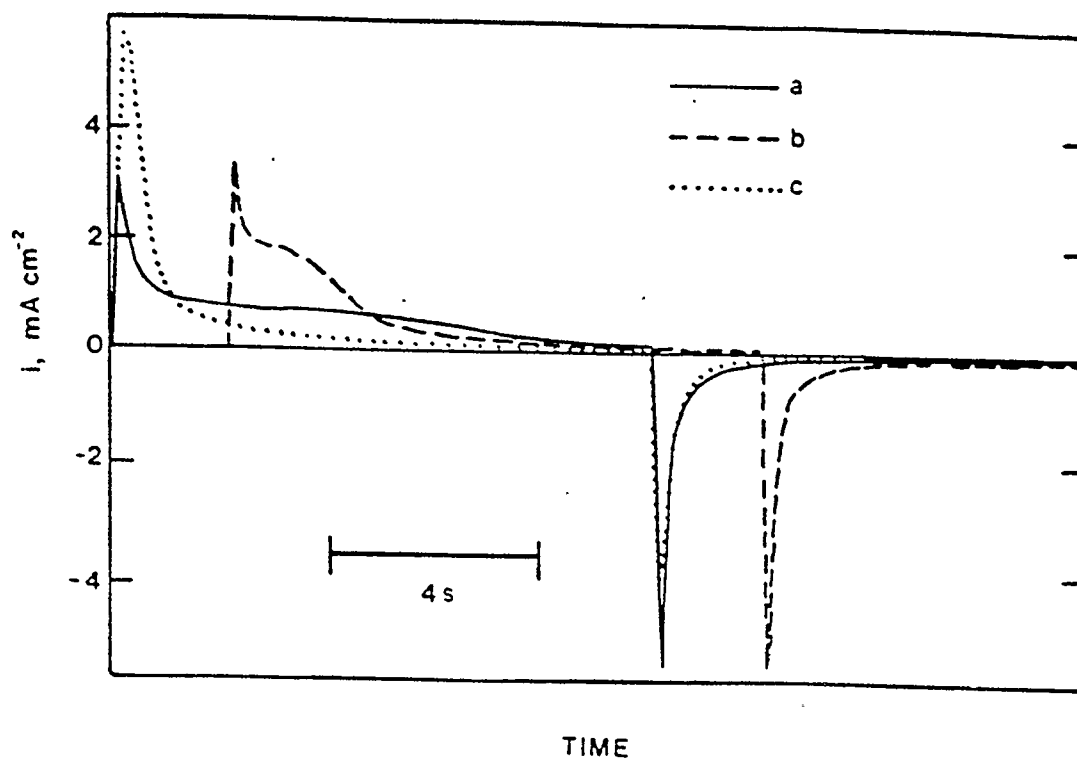


Fig. 7.6 The i vs. t plots for an oxide film at different $E(-)$, $E(+) = 1.35 \text{ V}$; (curve a) $E(-) = 0 \text{ V}$; (curve b) $E(-) = 0.5 \text{ V}$; (curve c) $E(-) = 1.0 \text{ V}$.

peak was broader if the potential was held at $E(-)$ for a long time. This can also be explained by a more complete film reduction and thus a higher film resistance.

The film conductance, as seen by the disappearance of the i/t peak, could be improved by applying relatively narrow potential pulses successively. This is illustrated in Fig 7.7. When a potential pulse with a width of 10 s was applied repeatedly, the shape of the anodic transient became sharper with the number of potential steps applied. This response seemed to indicate that the film content reached a steady-state condition, so that after numerous short pulses of potential, the trapped ions and water caused the film to remain conductive in both the oxidized and reduced forms.

An attempt was also made to obtain D_{app} from the potential step method, in order to compare with D_{app} values obtained from CV experiments and from the literature. Generally, D_{app} calculations were carried out for the cathodic process, since the anodic process was complicated by the i/t peak.

Here, D_{app} can be obtained from the Cottrell equation [117],

$$I = nFACD^{1/2}/(\pi t)^{1/2} \quad (7.4)$$

i.e. from the slope of an (i vs. $t^{-1/2}$) plots (Fig. 7.5, curves a and b). In Fig. 7.5, both plots are linear but do not intersect the origin. By using the same treatment as in section 7.1, equation (7.4) can be rewritten as

$$I = Q_c D^{1/2} / d(\pi t)^{1/2} \quad (7.5)$$

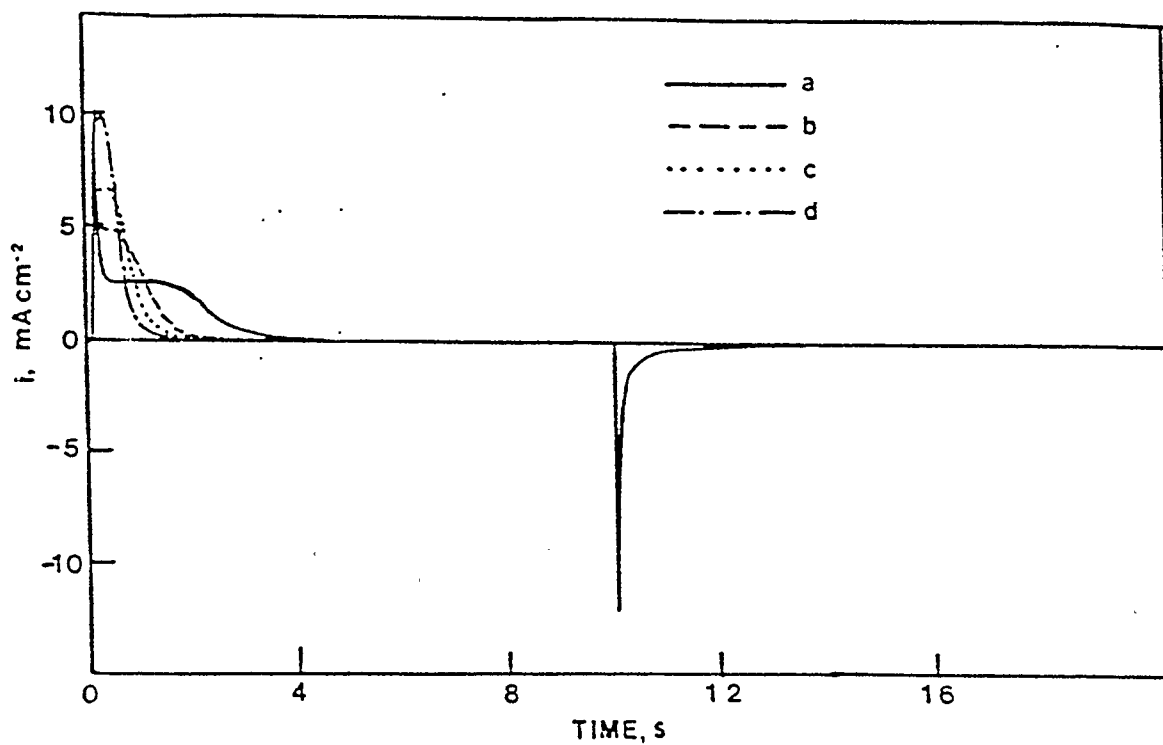


Fig. 7.7 The i vs. t plots for an oxide film, $E_{(+)} = 1.40$ V, $E_{(-)} = 1.0$ V; pulse = 10 sec. (curve a) first pulse; (curve b) 2nd pulse; (curve c) 3rd pulse; (curve d) 5th pulse.

For example, in Fig. 7.5 (curve a), when $E_{(+)} = 1.45$ V, the slope of the $I-t^{-1/2}$ plot is ca. $1.03 \text{ mA s}^{1/2}$, and the cathodic charge (Q_c), determined coulometrically, is 1.5 mC . Q_t was estimated from CV to be 2.8 mC , from which d could be estimated, from Fig. 6.5, to be $4000 \text{ \AA}$. D_{app} is then $2.4 \times 10^{-9} \text{ cm}^2/\text{s}$. It is noteworthy that the Q used in equation (7.5) is the charge passed in the cathodic potential step (Q_c), which is smaller than the cathodic charge (Q_t) obtained from CV experiments. This is because Q_c is considered to correspond to the 'real' concentration of electroactive sites in the film, which operate electrochemically during the cathodic potential step. A detailed discussion of this phenomenon will be presented in Section 7.3.

A similar calculation applied for the same electrode but with a $E_{(+)}$ of 1.50 V (Fig. 7.5 curve b), led to the result that D_{app} equal to $2.6 \times 10^{-9} \text{ cm}^2/\text{s}$. Numerous calculations were carried out at these oxide electrodes with different thicknesses and $E_{(+)}$, and the D_{app} values have been found to be in the range of 1.0 to $8.0 \times 10^{-9} \text{ cm}^2/\text{s}$.

The D_{app} values calculated from CV experiments ($2.6 \times 10^{-9} \text{ cm}^2/\text{s}$) and from the i/t responses are very close. These values are also of the same order as D values obtained for Ir hydrous oxide films [111]. In the case of Ir, D values in this range were considered to be an indication that electron mobility within the film is the rds [111].

However, these D_{app} values are found to be about ten to

one hundred times greater than the D_{app} values obtained at polymer modified electrodes (ca. 10^{-10} to 10^{-11} cm²/s) [105,107,110,116]. In the latter case, D_{app} values vary with polymer structure, densities of the electroactive centers, solvent etc., and ion diffusion in the film is considered to be the rds [104-106,116]. If one assumes that electron hopping within the glassy alloy oxide film is fast, the ten to one hundred times larger D_{app} implies that the hydrous oxide film formed at the glassy alloy may have a more open, more flexible and less cross-linked structure than that of many of the polymer films at electrode surfaces.

Overall, the electrochemical behavior of the hydrous oxide film formed at the Ni-based glassy alloy electrode is found to have many similarities to those of electroactive polymer electrodes, despite the fact that it is composed mainly of inorganic species such as Ni and Co oxide. Because of these similarities and the ability of the film to swell and shrink rapidly as ions and solvent enter and leave the film, the term "inorganic polymer" can also be used to describe those oxide films, similar to Burke's description of hydrous Ir oxide films [68].

7.3 Oxide Disproportionation

By examining Figs. 7.4, 7.6 and 7.7, it can be seen that the anodic charge density (q_a) is greater than the cathodic charge density (q_c) under most conditions of $E(+)$, $E(-)$ and

pulse width. This was especially true when $E(+)$ was in the potential range where the anodic current maximum appeared in the i/t response. The relationship of the q_a/q_c ratio versus $E(+)$ is shown in Fig. 7.8 (curves a and b). A maximum in the q_a/q_c ratio is observed at $E(+)$ = 1.38 to 1.42 V, i.e. in the critical range of $E(+)$ values when the i/t maximum was seen and also in the potential of peak A₂ in CV experiments. The q_a/q_c ratio approached to unity at both low and high $E(+)$ values. Fig. 7.8 also shows that the charge ratio maximum occurred at a less positive potential with a thin oxide (curve a) than with either a thick oxide film (curve b), or a relatively thin film but lower $E(-)$ (curve c).

It is important to note that q_a is usually relatively large in the potential step experiments, and never exceeds the charge obtained in a slow sweep CV experiment. In contrast, q_c in the cathodic potential step is very small, as compared to q_a and relative to the cathodic charge in a CV experiment. It is also very important to note that the same charges and the same large q_a/q_c ratios continued to be obtained, even after many identical potential pulses were applied.

The large q_a/q_c ratios might indicate that oxide dissolution or the OER occurred during the anodic potential step. However, as Ni and Co are not soluble at applied potentials [44,83,97], and as the anodic charges do not increase with time of pulses, oxide dissolution is not

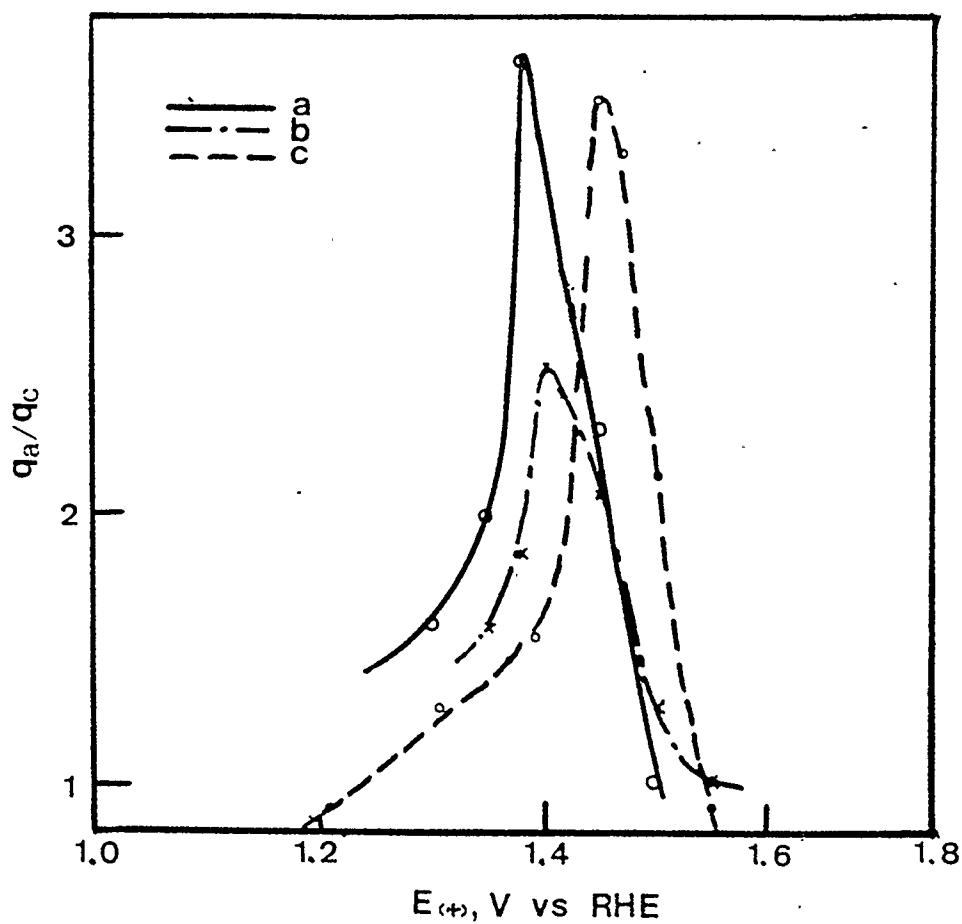


Fig. 7.8

The ratio of q_a and q_c versus $E(+)$ of potential step, $E(-) = 1.0$ V; (curve a) d is $500 \text{ \AA}$, (curve b) d is ca. $2000 \text{ \AA}$; (curve c) d is ca. $600 \text{ \AA}$, but $E(-) = 0$ V.

likely. Although, theoretically, the OER should occur at a potential of ca. 1.25 V, an overpotential is present, so that current corresponding to the OER can be seen only if an $E(+)$ is more positive than 1.45 V at these oxidized alloys. Also, since q_a is not greater than the cathodic charges in CV experiments, the influence of the OER on q_a must be considered to be negligible in the i/t experiments. One remaining explanation is that the cathodic charge becomes so low in the potential pulse experiment because of some concurrent oxide reduction processes, e.g. chemical oxide reduction.

In order to further investigate the oxidation and reduction of the oxide films during the potential stepping experiments, a combination of chronoamperometry and linear voltammetry was used. In Fig. 7.9, the electrode was first subjected to both anodic and cathodic potential steps, and q_a/q_c is ca. 2 (curve a). In curve b, the potential was scanned anodically at a sweep rate of 100 mV/s, and then stepped back to $E(-)$; q_a/q_c is now ca. 3. Alternatively, if the potential were stepped anodically and swept cathodically, a very similar q_a but much larger q_c would be obtained, with q_a/q_c close to unity (curve c). This result is very important because it demonstrates that there is no loss of charge during the anodic pulse, and that charge is lost during the reduction of the film.

Based on this result, further research was performed

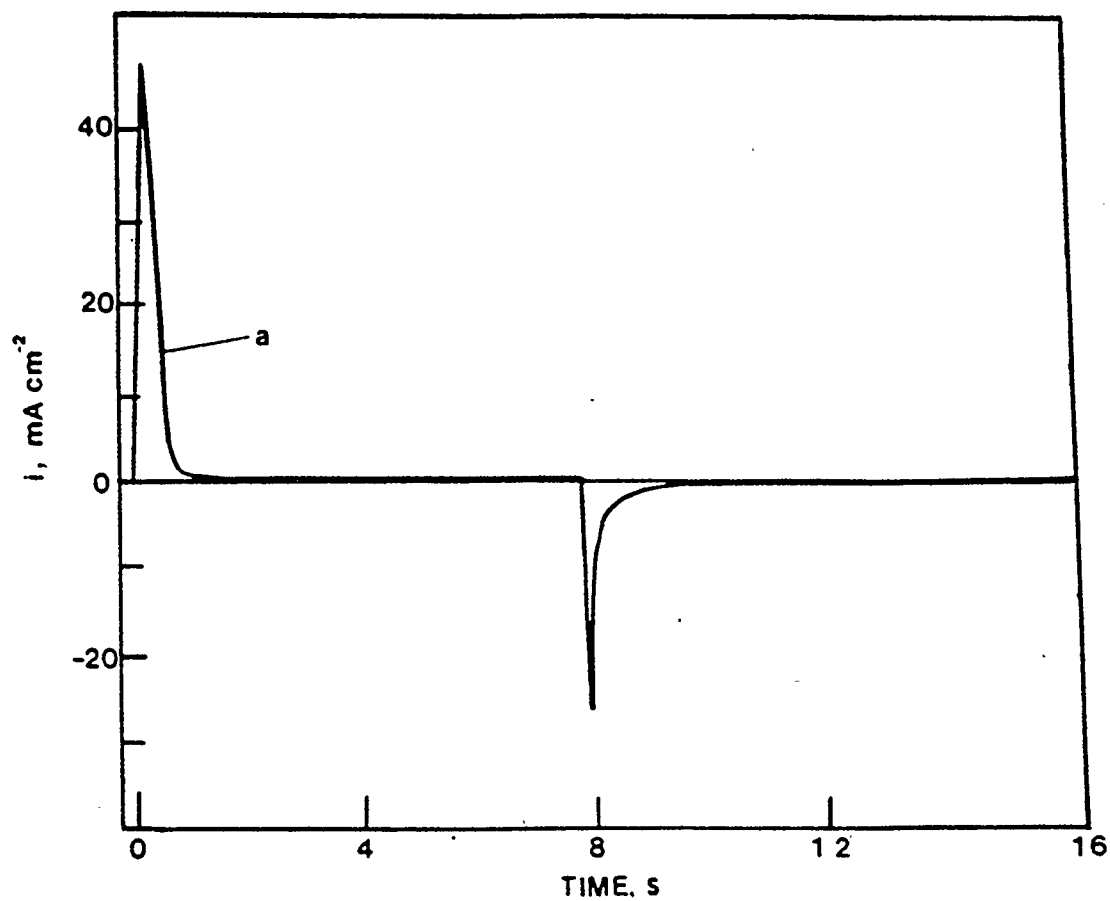


Fig. 7.9a

Combination of potential step and scan; $E(+)$ = 1.45 V, $E(-)$ = 0.98 V, s = 100 mV/s. (a) potential was stepped both anodically and cathodically.

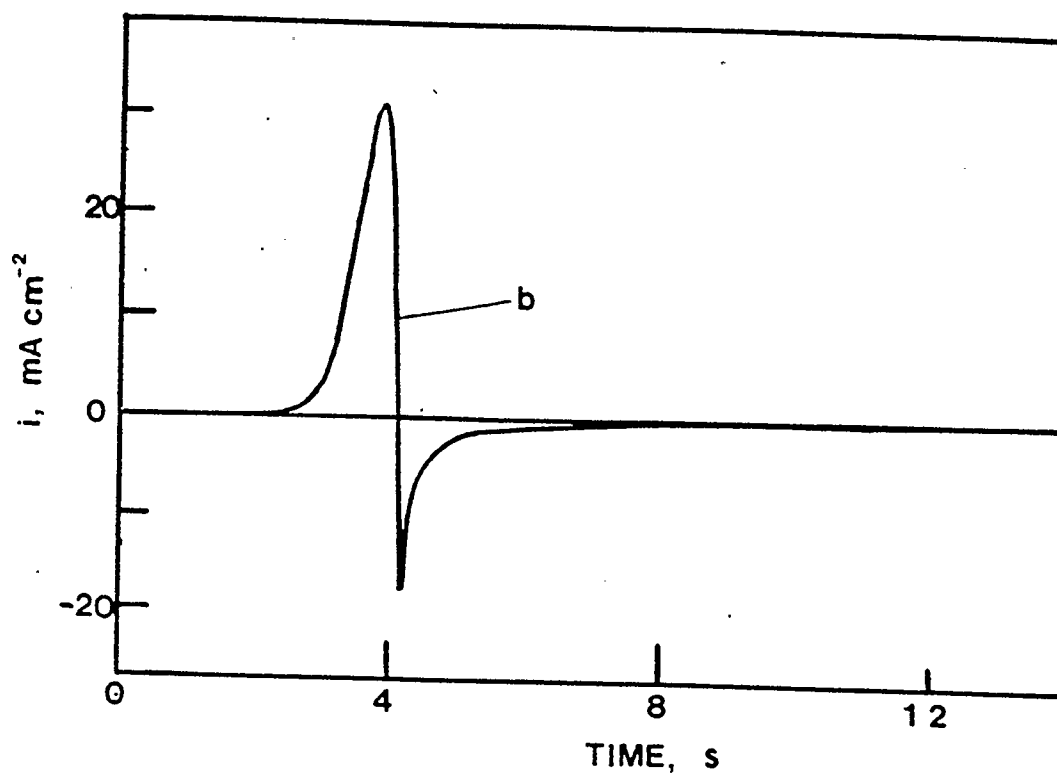


Fig. 7.9b

(b) potential was scanned anodically, stepped cathodically.

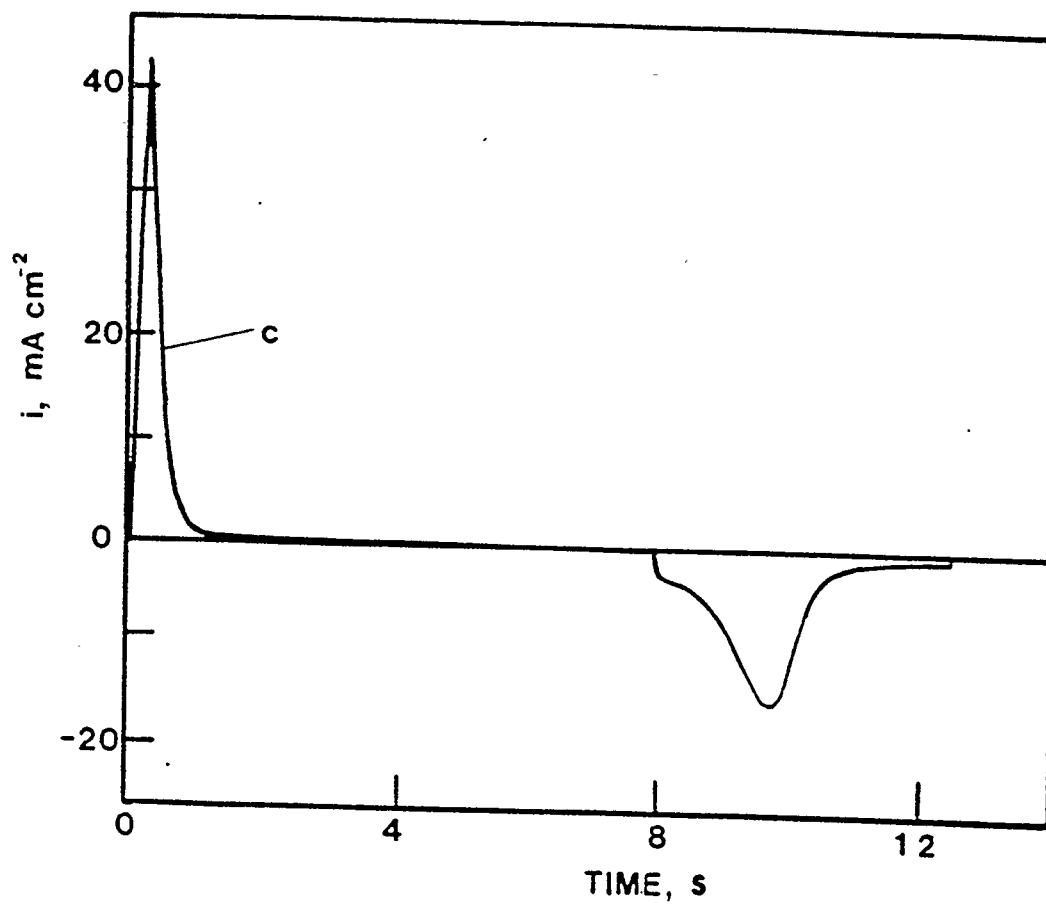


Fig. 7.9c

(c) potential was stepped anodically and scanned cathodically.

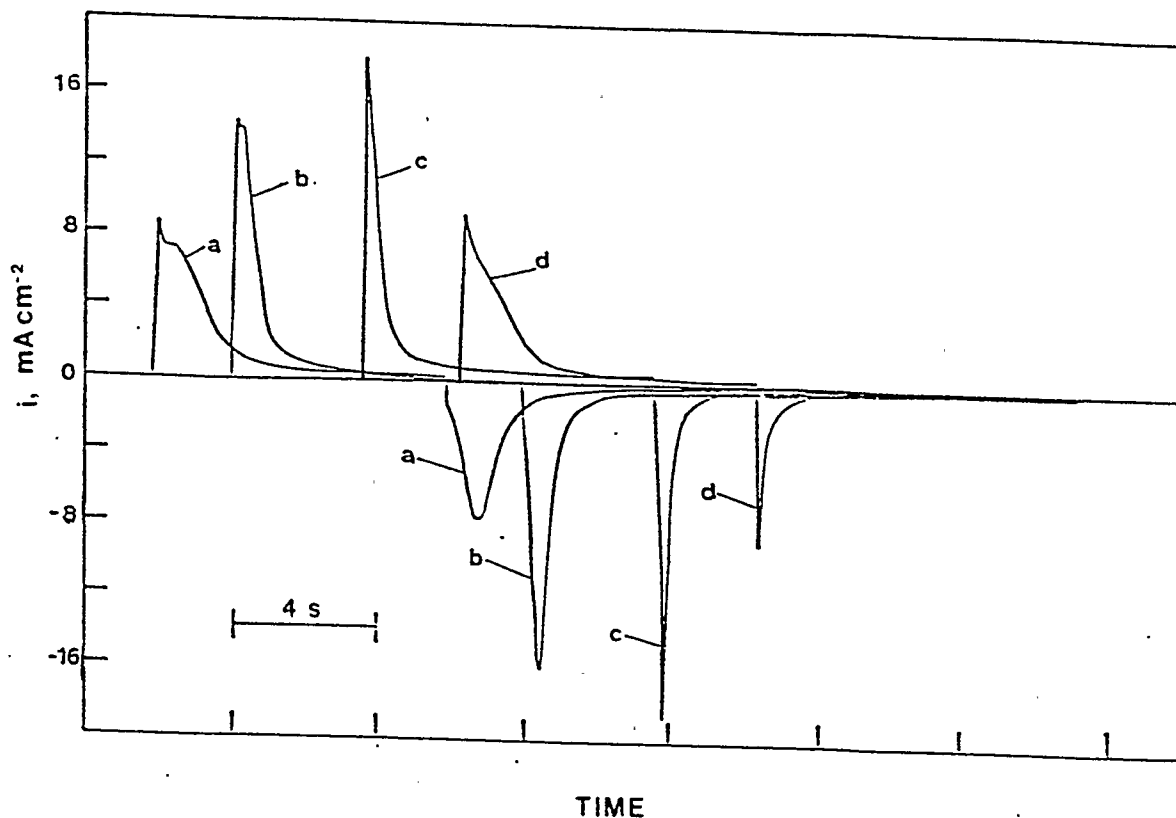


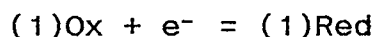
Fig. 7.10

i vs. t plots as a function of cathodic sweep rate, s_c . Potential was stepped anodically and scanned cathodically at various sweep rates, $E(+)$ = 1.38 V, $E(-)$ = 0.98 V; (curve a) s_c = 100 mV/s, (curve b) s_c = 200 mV/s, (curve c) s_c = 500 mV, and (curve d) s_c = 20 V/s.

focusing on the cathodic process. Fig. 7.10 demonstrates a series of anodic pulse/cathodic linear voltammograms, in which the potential was stepped anodically, but scanned negatively at different sweep rates. At low sweep rates (up to 500 mV/s), q_a/q_c is close to unity. q_c decreases significantly with increasing potential sweep rate, although q_a does not change.

An attempt was made to interpret the large q_a/q_c ratios obtained when a cathodic potential pulse was applied. One possible explanation is that the film reduces chemically as well as electrochemically during a cathodic pulse. It is suggested that the composition of the solution within the oxide film is not at equilibrium when it is rapidly reduced. Because the oxidation/reduction of the oxide involves the consumption/releasing of OH^- (reaction 6.3), it is possible that during the cathodic step, different parts of the film contain solutions of different pHs, so that a concentration cell (in terms of pH) develops within the oxide during its reduction.

To simplify the discussion, the oxide is considered to be divided into layers (Fig. 7.11). Each single layer may be several monolayers of the film. Electron transfer within this multilayer occurs via hopping from layer to layer, where (1), (2), (n) etc. indicate the layer number, commencing with the layer of oxide adjacent to the metal (1).



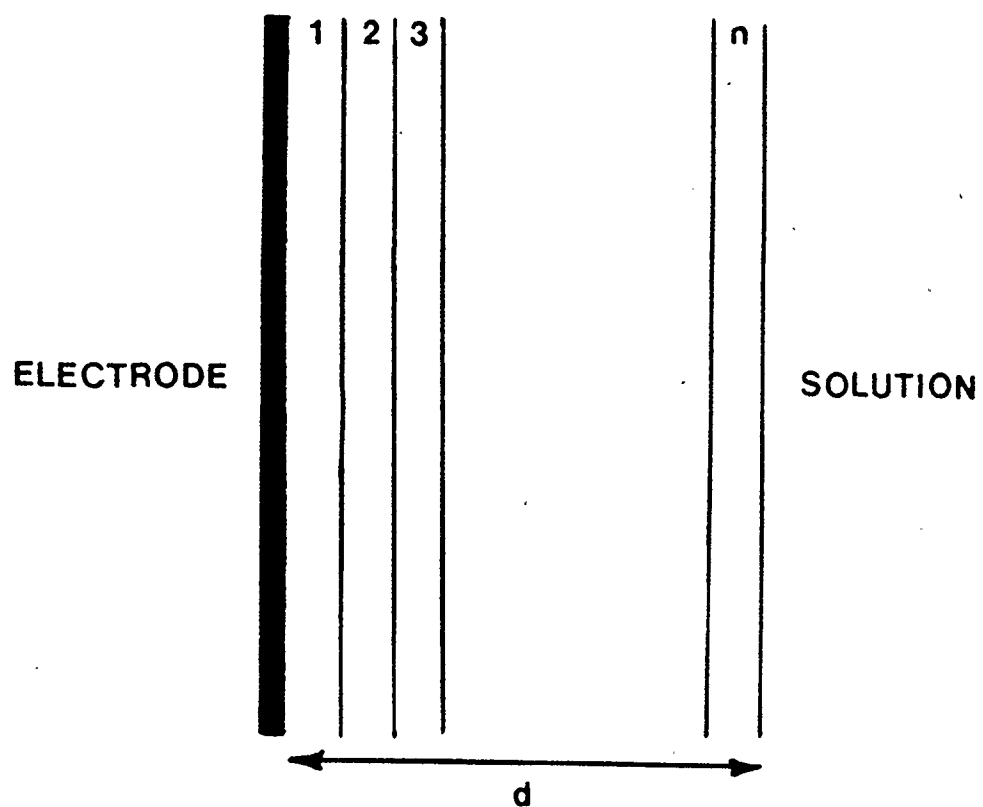
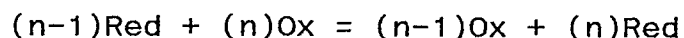
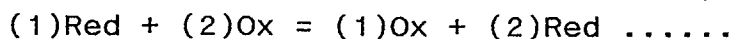
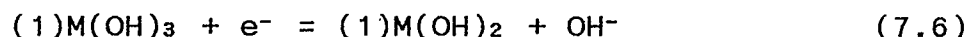


Fig. 7.11 A schematic of multilayer oxide film.



During the anodic oxidation of the film, electrons hop towards the underlying metal, and OH^- , Na^+ and a large amount of H_2O are injected into the film, as discussed in reaction (6.3). Therefore, at $E(+)$, the hydrous oxide film ($\text{M}(\text{III})$ oxide) can be considered to be full of ions and solvent (H_2O). The pH in the solution inside the film is assumed to be somewhat lower than the pH outside of the film (bulk solution), due to the consumption of OH^- in reaction (6.3).

When $E(-)$ is first applied, electrons are injected initially into the $\text{M}(\text{III})$ oxide film in layer 1. The hydrous oxide in this layer is then reduced, as in reaction (7.6).

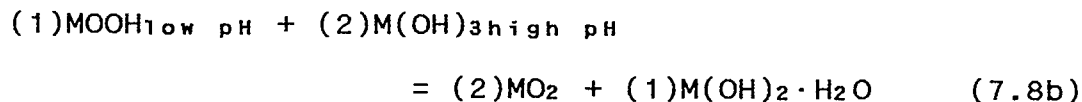
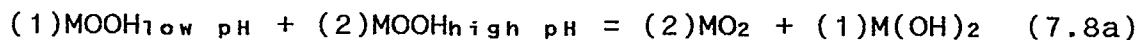


The OH^- will then begin to diffuse towards the solution. As more electrons are injected into the film, electrons will hop from layer 1 to layer 2. Also, as OH^- leaves the film, the oxide takes on a more dehydrated form

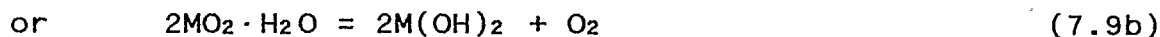


A similar process will occur in layer 3, etc, until the film is completely reduced. This overall process will cause a pH gradient across the film, with a lower pH further inside the film and a higher pH near the solution side of the film. It is known that metal oxides at low pH have higher E^0 values than in higher pH solutions, according to Pourbaix et al. [44,97]. Therefore, layer 1 and layer 2 (for example) can

form a "concentration cell", in which the metal sites in layer 1 (lower pH) could oxidize the metal sites in layer 2 (higher pH). It is assumed that M(III) sites are susceptible to this reaction, as oxidation states of M(II) and M(IV) are readily available within a narrow potential range, i.e.



MO₂ would be a mixture of NiO₂ and CoO₂, which are considered to be very unstable and will decompose rapidly, producing O₂ and either M(II) or M(III) oxides [44,97,101], i.e.



In this way, some M(III) is reduced to M(II) oxide via a disproportionation reaction. That is, H₂O reduces the M(III) oxide to M(II) oxide, as opposed to an electron from the underlying metal electrode. This type of process does not appear to occur during the anodic pulse. If a concentration cell of this type did develop, then the anodic charge observed in a pulse experiment would be greater than the charge observed in the CV experiment. This is not observed. It is possible that the disproportionation reaction occurs only when M(III) oxide, having a higher and lower oxidation state readily available, is the majority species in the film.

The above discussion involves only one of several disproportionation models which could explain the anomalously

low charge densities observed during oxide film reduction via a cathodic pulse. Other models could involve oxide reduction from the oxide/solution interface inwards, and a pH gradient in the reverse direction within the film,

Chapter 8

CONCLUSIONS AND FUTURE RESEARCH

8.1 Conclusions

The following conclusions can be drawn from this work:

1. Cr is enriched at the surface of both "as-quenched" glassy alloys 1 and 2, but is dissolved in alkaline solutions at positive potential.
2. In pH 14 solutions, a microporous, hydrous Ni-based oxide can be formed on the surface of the glassy Ni-Co alloy, with the use of potential cycling techniques. The film appears to be chemically homogeneous and has special properties which are different from those of Ni or Co electrodes.
3. Electrochemically, the CV wave of the glassy alloy 1 appears quite similar to that of polycrystalline Ni electrodes, but with the following new features:
 - a) a much faster oxide growth rate than either Ni or Co electrode;
 - b) an inhibition of the HER at low overpotentials, which was not observed at either Ni or Co electrode;
 - c) loss of the M/M(II) oxide (M = Ni,Co) transformation peak after the first cycle of E;
 - d) peculiar chronoamperometric behavior very similar to polymer electrodes which was not seen at either Ni or

Co electrodes;

e) much more visible electrochromic behavior and interference color changes.

4. The mechanism of the hydrous oxide growth is considered to be analogous to the mechanism of Ir hydrous oxide formation. In both cases, a maximum of one monolayer of hydrous oxide film can be formed on the surface of the electrodes in a single sweep of potential.
5. Microscopically, the glassy alloy 1 oxide shows a smooth, noncrystalline, mud-cracked structure, typical of hydrous oxide films. The surface appears much smoother than that of either Ni or Co polycrystalline electrodes.
6. The electrochemical behavior of the hydrous oxide film formed at the Ni-Co glassy alloy electrode shows many similarities to those of electroactive polymer coated electrodes. Its oxidation and reduction are proposed to occur via electron hopping between neighboring metal ion sites, together with charge compensating counterions and solvent transferring into/out of the film.
7. Apparent diffusion coefficients are obtained for the film from both CV and potential step experiments. D_{app} is found to range between 1 and 8×10^{-9} cm²/s, similar to hydrous Ir oxide films. The oxidized form of the film is believed to be swollen and full of ions and solvent. It appeared to be less resistive than the deswollen, more cross-linked reduced form of the film.

8. In the potential step experiments, film reduction occurs both electrochemically and by another parallel process. It is suggested that a pH gradient is established in the film, leading to an M(III) oxide concentration cell. This results in the disproportionation of M(III) oxide to M(II) and M(IV) oxide. Decomposition of M(IV) oxide to M(II) oxide with release of O₂ is considered to occur. Therefore, some of the M(III) oxide may be reduced chemically.
9. The oxide film appeared to inhibit the HER at low overpotentials, but this inhibition is lost at overpotentials of ca. 300 mV.
10. The oxide has a low Tafel slope (45 ± 5 mV/decade cd) for OER. It seems the oxide is a good catalyst for oxygen evolution.
11. Compared with the "as-quenched" glassy alloy 1, the electrochemically oxidized glassy alloy 1 has a higher open circuit potential in alkaline solutions (with and without chloride ions), and initially appeared to serve as a barrier towards chloride ions at anodic potentials. However, as the oxide film is oxidized, chloride ions appear to enter the oxide and cause pitting of the underlying metal.
12. The electrochemical behavior of the Co-based alloy (alloy 2) also appeared to be different from that of the pure Co metal electrodes, in terms of disappearance of the

M/M(II) oxide transformation peak in the CV, more visible electrochromic behavior and interference colors, and inhibition of the HER at low overpotentials.

8.2 Recommended Future Research

The following topics are suggested for future research on Ni and Co-based glassy alloys:

1. the electrochemical behavior of Co in alkaline solution, and how it influences the electrochemistry of the glassy alloy;
2. the cause of the "shoulder" on peak A₂ in CVs of alloy 1 when thick oxides are present;
3. detailed kinetic study of the electrochemically formed hydrous Ni-Co oxide, especially in terms of theoretical treatments, to enrich the theory of hydrous oxides;
4. further study of the influence of interactions on CV wave shapes of the alloy 1;
5. detailed study on Co-based glassy alloy 2.

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