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Structure, composition and pitting behavior of sputtered Al base, Fe base, and Ni base alloy films

Inturi, Rama Brahmam, Ph.D.
The Ohio State University, 1993
STRUCTURE, COMPOSITION AND PITTING BEHAVIOR OF
SPUTTERED AI BASE, Fe BASE, AND Ni BASE ALLOY FILMS

DISSERTATION

Presented in partial fulfillment of the requirements
for the degree Doctor of Philosophy in the
Graduate School of the Ohio State University

By
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The Ohio State University
1993

Dissertation Committee:
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Approved by
Adviser
Materials Science and Engineering
The heart has its own reasons which reason do not know

------- Blaise Pascal (1623-1662)

What is most needed for learning is an humble mind

------- Idem The book of history

Dedicated to
My late parents, loving brother, and affectionate grand parents
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Chapter 1
Introduction

Pitting is one of the most dangerous and most common types of metal corrosion. It is localized, intense, and exceedingly destructive since pits can either cause perforation or act as crack nucleation sites in materials. It often goes unnoticed until failure occurs, since most of the metal is in passive state and corrosion takes place only on a small fraction of the metal. It represents an important limitation for the safe and reliable use of many metallic materials in various industries.

Ironically, pitting is an adverse side effect of a beneficial phenomenon of passivity. It is established that pitting and other types of localized corrosion processes occur as a result of the localized breakdown of the passive film which covers a given metal or alloy. Most commonly, aggressive species such as chloride and other halide anions cause this breakdown in aqueous environments. A number of structural materials such as aluminum alloys, iron base alloys, and Ni base alloys are susceptible to pitting in sea water and other chloride containing environments. An idealized anodic polarization curve for a system exhibiting passivity is shown in Figure 1. This diagram can be divided into three regions, namely, active, passive, and transpassive regions. In the active region, as the potential (driving force for the reaction between metal and environment) is increased in the positive direction from the open circuit potential ($E_{ocp}$), the current density increases until a critical value $i_c$ (the critical
Figure 1  Idealized anodic polarization curve for a metallic system exhibiting passivity (ref. 1)

- $E_{ocp} =$ Open circuit potential
- $i_c =$ Critical current density required for passivation
- $E_p =$ Primary passive potential or Flade potential
- $i_p =$ Passive current density
- $E_{np} =$ Pitting potential
current density for passivation) is reached. At the potential $E_p$, the current density drops suddenly to a much lower value $i_p$, the passive current density. In the absence of damaging species such as chloride ions the current density continues to be low until the beginning of the transpassive region. However, in the presence of chloride species, the current density increases abruptly at the potential, $E_{np}$ which is much lower than the transpassive potential. At this potential, pits nucleate and begin to grow. The potential $E_{np}$, known as the pitting potential or pit nucleation potential is an important parameter by which the susceptibility of metal or alloy to pitting corrosion can be measured. The other relevant parameter, characterizing the pitting phenomena, the induction time for pit initiation can be obtained from the current density vs. time plots determined at constant anodic potential.

The pitting process is generally autocatalytic in nature. The corrosion processes occurring in a pit produce conditions that stimulate the activity of the pit. The rapid dissolution of the metal in the pit generates an excess of metal ions. The hydrolysis of metal ions results in a build up of a high concentration of hydrogen ions. These hydrogen ions stimulate the dissolution of most metallic materials and the entire pitting process accelerates with time. It is generally acknowledged that the pitting susceptibility of metals and alloys is related to the quality of the passive film covering the metal. The passive film characteristics such as its composition, structure, thickness, electrical and mechanical properties, adherence and adsorption aspects have been correlated to the pitting resistance of the materials. Several theories have been proposed to explain the damage of the passive films by halide ions. These models along with the experimental observations are described in Chapter II (Literature Review).
In recent years, a number of advanced materials processing methods have been employed to improve the general and localized corrosion resistance of metallic materials. These methods include rapid solidification, mechanical alloying, physical vapor deposition processes such as sputtering, ion-beam surface modification techniques, electrodeposition, electroless deposition and laser processing. The benefits of using these methods are (i) improvement in the degree of homogeneity and reduction / elimination of impurity segregation; (ii) elimination / reduction of second phases in the microstructure; (iii) the ability to obtain amorphous structures; (iv) the ability to produce supersaturated alloys containing high concentrations of passivity enhancing elements. Since a series of alloying elements can be incorporated in a parent metal by the non-equilibrium methods without forming second phases, the effect of alloying elements on pitting corrosion of metals can also be conveniently studied. The details of the processing methods and the corrosion characteristics of the metastable alloys prepared by these methods are presented in Chapter II (Literature Review).

Al alloys produced by conventional methods contain multiple phases and a lot of impurities, hence they are prone to localized attack. Since Al has limited solubility for passivity enhancing elements, the passivity of Al can not be enhanced by conventional alloying methods. In the last few years, the above non-equilibrium methods have been used to obtain 'stainless aluminum' with high resistance to localized corrosion.

Even though several new materials with superior corrosion performance have been developed, it is possible to further increase the corrosion resistance to higher limits by choosing the proper processing method and controlling the process variables and the material composition. The theories proposed to explain
the pitting behavior of metastable Al alloys are not applicable to other alloy systems and suffer from several weaknesses. Also, these models are not consistent with the experimental observations. The structural investigations of the alloys prepared by the unconventional methods are not complete. Therefore, this research program was carried out critically addressing all of the above issues.

The objectives of this research project are as follows:

(1) Preparation of 'stainless Al' (supersaturated Al-Cr and Al-Ta) alloys and sputtered Fe base and Ni base alloy films with high pitting resistance

(2) Determination of composition, structure and anodic polarization behavior of the above alloys

(3) A mechanistic description of the effect of alloying elements on pitting corrosion of Al, Fe, and Ni.

Subsequent chapters have been organized in the following manner.

Chapter II: A review of literature on corrosion behavior of non-equilibrium metallic materials and mechanisms of pit initiation (both general and specific to Al base, Fe base and Ni base alloys)

Chapter III: Experimental procedure

Chapter IV: Results

Chapter V: Discussion

Chapter VI: Conclusions

REFERENCES
Chapter II
Literature Review

2.1 Non-equilibrium, corrosion resistant alloys

The corrosion behavior of metallic materials is strongly influenced by their chemical composition and structure. The size, shape and distribution of second phases, impurities, inclusions, structural and chemical characteristics of grain boundaries, presence of texture and other crystalline imperfections, which determine the corrosion performance, depend on the extraction technology, materials processing (forming, welding etc.) and heat treatment. Even though the alloying elements such as Cr and Mo increase the breakdown potentials of metals (especially steels) significantly, the localized corrosion of the alloys is still limited by the presence of a large number of structural and chemical inhomogeneities. These inhomogeneities mainly arise due to the presence of grain boundaries, dislocations, flaws and macro-defects, inclusions, second phase precipitates, solute depleted zones and induce the formation of weak spots in the passive film facilitating the breakdown of the passive film at these weak spots. Processing techniques such as strip casting and thermo-mechanical treatment are found to marginally increase the pitting resistance of Al alloys through a microstructural modification. Since the mid-1970's, a number of new metals and alloys with extraordinarily high corrosion resistance were obtained by a variety of non-equilibrium processing methods. Examples of these methods are (i) rapid solidification, (ii) mechanical alloying, (iii) sputtering, (iv) ion
beam surface modification techniques, (v) electro-deposition and electroless-deposition and (vi) laser processing. Through these methods, it is possible to obtain chemically, structurally homogenous alloys supersaturated with beneficial alloying elements that promote passivity. Processes (iii) to (vi) can be used to obtain corrosion resistant coatings on metal surfaces unlike the techniques (i) and (ii). A description of the chemical, structural, and electrochemical characteristics of the materials processed by each of the above methods are given below.

2.1.1 Rapid Solidification:

Metallic alloys produced by rapid quenching (cooling rates are of the order of $10^6$ degree C/sec) from the liquid state exhibit technologically interesting physical (mechanical, magnetic) and chemical properties. In specific alloy systems and in certain ranges of alloy compositions glassy metals can be produced. Because of the required quenching rates, glassy metals are necessarily produced in the form of filaments, wires, or thin sheet. The alloys consolidated from either rapidly quenched thin strips or rapidly solidified powders loose amorphous nature and are usually microcrystalline in nature. The corrosion behavior of both amorphous metals and microcrystalline alloys, as determined by several investigators will be presented here.

2.1.1.1 Metallic Glasses:

Amorphous alloys are free from defects associated with crystalline state such as grain boundaries, dislocations, and stacking faults. They are also free
from chemical defects such as second phases, precipitates and segregates, which are normally produced by solid state diffusion during slow cooling or heat treatment. The amorphous alloys are therefore structurally and chemically homogeneous with respect to surface related characteristics such as corrosion. Metallic glasses can be categorized into two groups; (a) Metal-Metalloid type, and (b) Metal-Metal type.

2.1.1.1(a) Metal-Metalloid type: A number of Fe, Ni, Co and Ti base amorphous alloys containing large quantities of one or more metalloid elements such as P, B, C, and Si have been prepared since 1970. Metalloid elements are necessary structural components of the metallic glasses and plays a significant role in the amorphous phase formation. The corrosion rates of Fe-Cr-13P(13 at% P) -7C and Ni-Cr-15P-5B alloys estimated from the weight loss measurements in chloride solutions at 30 C are shown in Figures (2) and (3), respectively. For comparison purposes, the corrosion rates of crystalline Fe-Cr alloys are also presented in Figure 2. The data in Figure 2 indicate that the corrosion rates of amorphous alloys are initially higher than crystalline alloys, but sharply reduced to low values at higher Cr concentrations. Similarly, the corrosion rates of Ni based glassy alloys decrease rapidly with increase in Cr content. The amorphous Fe-10Cr-13P-7C and Fe-10Cr-5Ni-13P-7C alloys showed no measurable weight change in 1M HCl solution, unlike the conventional crystalline 18Cr-8Ni stainless steel (Figure 4). The potentiostatic anodic polarization curves determined for Fe base and Ni base glassy alloys in 1M H2SO4 and 1M HCl solutions are shown in Figures (5) and (6), respectively. The pitting potential of Fe-10Cr-13P-7C alloy is about 1 V_{SCE}, whereas the conventional Fe-10 at% Cr alloy exhibits a pitting potential of about 0.0 V_{SCE}. The amorphous Ni-Cr-15P-
Figure 2 Comparison of corrosion rates of amorphous Fe-Cr-13P-7C alloys and crystalline Fe-Cr alloys in 1 N NaCl at 30 C (ref. 4)
Figure 3 Change in corrosion rate of amorphous Ni-Cr-15P-5B alloys in 10% FeCl$_3\cdot$H$_2$O at 30 C with the Cr content (ref. 4)
Figure 4  Comparison of corrosion rates of amorphous Fe-10Cr-13P-7C and Fe-10Cr-5Ni-13P-7C alloys and crystalline 18Cr-8Ni stainless steel as a function of HCl concentration at 30°C (ref. 4)
Figure 5  Potentiostatic polarization curves of amorphous Fe-10Cr-13P-7C alloy in 1M H$_2$SO$_4$ and 1N NaCl (ref. 4)
Figure 6  Potentiostatic polarization curves of amorphous Ni-Cr-15P-5B alloys in 1M H₂SO₄ and 1N NaCl (ref. 4)
5B alloys containing 7 - 9 at% Cr show a wide passive region and a critical pitting potential does not appear even in 1 M HCl^4.

The passivating ability and the corrosion resistance of the amorphous metal-metalloid alloys are largely dependent on the nature and the concentration of constituting elements^6,7. The metalloids affect both the kinetics of passivation and the composition of the passive film^6,8,9,10. The beneficial effect of the metalloid in improving the corrosion resistance decreases in the order P, C, Si and B^6. The amorphous P-bearing alloy dissolves rapidly before the alloy forms a stable surface film and, therefore, they have the highest ability to accumulate beneficial species in the passive film. The composition of the passive film on Fe-Cr-P alloys was determined to be a more protective hydrated Chromium oxyhydroxide^11. According to Hashimoto^8,9 and Janik-Czachor^10 phosphorous undergoes oxidation and is present in the passive film as phosphate anions. Carbon present in amorphous alloys does not greatly accelerate the passive film formation and is also not contained in the film since most of the metal carbonates in the film are generally soluble^6 in the film. Si and B also do not highly accelerate the formation of passive film, but they tend to be contained in the passive film as silicate and borate, respectively^6.

The metallic alloying elements can be classified into three groups, depending on their roles in increasing the corrosion resistance. Cr forms its own passive film and is observed to be the most effective alloying element in improving the corrosion resistance of amorphous alloys. Figure 7 shows the anodic polarization curves determined for Fe-xCr-13P-7C alloys in 1N H_2SO_4
Figure 7  Linear Sweep voltammograms (LSV) of glassy Fe-Cr-13P-7C alloys in 1 M H₂SO₄ at 303 K (ref. 12). The numbers refer to the atomic concentration of Cr.
with Cr content varying from 1 to 10 at%\textsuperscript{12}. The active region almost disappears for Cr contents greater than 8 at%.

The second group includes the alloying elements such as Mo, W, V, Nb, Ta and etc., which are more active than the main metallic component (example: Fe) of the alloys. The surface films consisting of the cations of these elements are more stable than the films containing only the oxidized species of Fe. The surface films are therefore enriched with the oxidized species of the elements of this group and act as diffusion barriers for active dissolution of the alloys\textsuperscript{13,14}. As a result, the passivating species of Cr will be accumulated. The beneficial effects of these elements can easily seen from Figure 8.

The third group of alloying additions include elements such as Ni, Co, Cu, Ru, Rh, Pd, Pt etc. which are more noble than Fe that is present in the Fe based alloys. The oxidized species of these elements are chemically unstable and do not exist in the passive films. It is suggested that Ni addition in a Fe-Cr-P-C alloy promotes the formation of chromium oxyhydroxide in the passive film\textsuperscript{6}.

The high localized corrosion resistance of the amorphous alloys has been attributed to (1) protective quality, (2) high uniformity, and (3) rapid formation of the passive film. According to X-ray Photoelectron Spectroscopic studies\textsuperscript{11}, passive films on amorphous alloys mainly contain hydrated chromium oxyhydroxide, \(\text{CrO}_x(\text{OH})_{3-2x}\cdot n\text{H}_2\text{O}\) similar to the passive films on crystalline Fe-Cr alloys and stainless steels. However, the concentration of the oxidized species of Cr is much higher in amorphous alloys.
Figure 8  Anodic polarization curves produced by additions of various extra metallic alloying elements in amorphous Fe-Cr-P-C alloys (ref. 15)
The passive films on amorphous alloys are chemically and structurally homogeneous. The composition of the passive film on Fe-Mo-metalloid alloys is found to be hydrated iron oxyhydroxide and these alloys were found to be passivated even in 1 M HCl. On the other hand, the crystalline Fe-Cr alloys and stainless steels can not be passivated in 1 M HCl even though the passive film in those alloys is hydrated chromium oxyhydroxide. Hashimoto et al\(^4\) concluded that the protective properties of hydrated iron oxyhydroxide present in the passive film on amorphous alloys are due to its uniformity. In other words, the protective nature of the passive film is determined not only by the composition but also the uniformity of the passive film. The authors arrived at the same conclusion by comparing the passive films on amorphous Fe-Cr- P-C alloys to those obtained on the crystalline materials (obtained by heat treating the amorphous alloys) with the same composition.

From the current density vs. time plots, it has been determined that the amorphous Fe-Cr-P-C alloy is more reactive than the 18Cr-8Ni stainless steel, before passive films exist on the surface. The high reactivity of the amorphous alloy provides the rapid enrichment of passivating species at the alloy / film interface and the rapid formation of the passive film. Metalloids such as P, B, C, and Si stimulate the active dissolution of the alloy, which is necessary prior to the passive film formation.

2.1.1.1 (b) Metal - Metal type: Examples of the amorphous materials in this category are Cu\(_{50}\)Zr\(_{50}\)\(^{15}\), Cu\(_{50}\)Ti\(_{50}\)\(^{15}\), Fe\(_{70}\)Si\(_{30}\)\(^{15}\), Fe-Cr-Zr\(^{16}\), Co-Cr-Zr\(^{16}\), Al-Ln-Tm\(^{17}\) and Mg-Ln-Tm\(^{17}\) (Ln-Lanthanide metal, Tm - transition metal) alloys. It was determined that the corrosion performance of Cu-Zr, Cu-Ti, and Fe-Si glassy
alloys are definitely higher than that of the crystallized alloys of same composition. However, the corrosion behavior is primarily dependent on the content of the constituting element having the highest corrosion resistance. The passive current density of glassy Cu-Ti and Ni-Ti\textsuperscript{18} alloys was reduced by the addition of small amounts (of the order of 5 at\%) of P. The corrosion rates of amorphous Fe-Cr-Zr and Co-Cr-Zr alloys in chloride solutions were observed to be higher than those of Fe-Cr-13P-7C and Co-Cr-13P-7C alloys, respectively containing the same amount of Cr. Additions of W and Mo were found to be effective in significantly lowering the corrosion rates of Fe-Cr-Zr alloys similar to the case of Fe-Cr-P-C alloys. The amorphous phase in the Al-Ln binary system is formed, when the concentration of Ln is varied from 7 at\% to 15 at\%. The addition of a transition element to Al-Ln alloys brings about a significant extension of glass formation ranges. The corrosion resistance of the amorphous Al-Y-Ni and Mg-Y-Ni alloys were found to be superior to that of conventional Al and Mg alloys, respectively.

Although the metallic glasses are interesting from a research stand point, two obvious limitations are apparent from their practical application in industries. Firstly, crystallization or devitrification\textsuperscript{19} can occur at elevated temperatures resulting in a loss of corrosion performance. The second limitation is concerned with the physical dimensions of the materials product. Because of the high cooling rates required, at least one dimension of the alloy should be very thin. To overcome the first limitation, the composition has to be adjusted so that the amorphous alloys can have high glass transition temperature. Because of the
second limitation, glassy metals are necessarily used as corrosion resistant coatings.

2.1.1.2 Microcrystalline alloys:

In this category, alloys of virtually any composition can be produced by rapid quenching methods. The grain size of these alloys is typically of the order of 1\(\mu\). The uniform and localized corrosion properties of the microcrystalline Al alloys and stainless steels were determined by several investigators. The microstructure and the pitting behavior of several rapidly solidified Al alloys containing Mg, Ti, Mn, Cr, Fe, Ni, Cu, Zn, Zr, Nb and/or Si in deaerated 0.5 N NaCl at 30 \(^\circ\)C was evaluated by Yoshioka\(^{20}\) et al. These alloys contain significantly reduced amounts of second phases and at times consist of a single phase. Highest pitting resistance was obtained for the case of Al-6 at% Mn and Al-6at%Ni-5at% Si and Al-6 at%Cr-5 at%Si alloys. In another study Fe\(^{21,22}\) and Er\(^{21}\) additions were found beneficial in increasing the pitting potential of Al. The microcrystalline 2024 Al alloys\(^{23}\) exhibited superior pitting resistance when compared to the conventional alloys of same composition. Additions of Ti\(^{24}\) and Ti-Ce\(^{24}\) (or V or Mo) to Al increased slightly the pitting potential of Al, however they decreased the passive current density by two to three orders of magnitude. Since the sputtered Al-Ta and Al-W alloy films exhibited significantly higher pitting potentials compared to that of Al, the authors\(^{25}\) prepared dilute bulk Al-Ta and Al-W alloys (maximum concentration of W or Ta is 1 at%) expecting a superior pitting resistance of the alloys in the bulk state. Firstly, rapidly solidified alloy powders were obtained by an atomization process and then dynamically consolidated. The consolidation process utilizes shock waves generated by
explosives to cause interparticle melting and bonding. The objective of this process is to discourage the precipitation of second phases. The x-ray diffraction and SEM studies performed on powders reveal the presence of precipitates $\text{Al}_3\text{Ta}$, $\text{Al}_5\text{W}$, and $\text{Al}_{12}\text{W}$. Anodic polarization of the consolidated alloys was found to be similar to pure Al. The poor performance of the alloys has been correlated with the presence of second phases present in the powders, and not to the consolidation process. The microcrystalline stainless steels$^{26,27}$ were found to be more resistant to pit initiation and propagation and the pits were easily passivated compared to the case of conventional stainless steels. Even though B is known to promote formation of metastable phases, the addition of B in rapidly solidified precipitation hardening stainless steels caused the depletion of Cr in the matrix making it susceptible to pitting corrosion$^{26}$. This problem was overcome by Ti additions which resulted in precipitation of Titanium borides causing negligible Cr depletion$^{26}$. The high pitting performance of the microcrystalline Al alloys and stainless steels has been primarily attributed to improved homogeneity and reduced segregation of impurities$^{27}$.

2.1.2 Mechanical Alloying:

Mechanical alloying (MA) has been successfully used to obtain microstructures with fine dispersoids of stable second phase particles within a fine grain sized matrix. In favorable cases, nanocrystalline grain sizes can be obtained. Metastable phases and a supersaturated solid solution have been observed in mechanically alloyed $\text{Cu-W}^{28}$ and $\text{Ag-Cu}^{29}$ systems, respectively. In recent years, amorphous alloys in metal-metal (example: $\text{Ni-Zr}^{30}$, $\text{Cu-Ta}^{31}$, Mg-Ni$^{32}$, $\text{Cu-Ti}^{33}$, soft magnetic alloys$^{34}$) and metal (Fe)-metalloid (C, B, Si, P)
systems\textsuperscript{35,36} have been synthesized by mechanical alloying. Additions of 5-10 volume % of ceramic particles such as alumina powder have been found to accelerate the formation of the amorphous phase in Fe-metalloid systems\textsuperscript{35,36}. The concentration of metalloids required for MA-induced amorphization is considerably higher than those required for the amorphization alloys prepared by rapid quenching\textsuperscript{35,36}.

The literature concerning the corrosion behavior of amorphous and nanocrystalline alloys produced by MA was not found. However, a few studies were performed to evaluate the corrosion behavior of dispersion strengthened MA Al alloys\textsuperscript{37,38}. The pitting potential of MA Al alloys was determined to be the same as that of conventional alloys\textsuperscript{37}. However, the open circuit potential of MA alloys is considerably lower and the separation between the pitting potential and corrosion potential becomes greater compared to that in conventional alloys. The pits on MA alloys were observed to be smaller in diameter, shallow, and nearly hemispherical in shape. The MA Al alloys contained homogeneously dispersed carbides (Al\textsubscript{4}C\textsubscript{3}) and oxides (Al\textsubscript{2}O\textsubscript{3}) in a fine subgrain microstructure with low angle grain boundaries. The carbide and oxide particles (average particle size \textasciitilde 100 Å - 300 Å) stabilize the sub-micron grain size. McIntyre\textsuperscript{37} claimed that Al\textsubscript{4}C\textsubscript{3}, when exposed to aqueous environment dissolves rapidly in water to form CH\textsubscript{4} and Al(OH)\textsubscript{3}. Al(OH)\textsubscript{3} thus generated would repassivate the incipient pits. Fine grained MA Al-Li-Mg alloys have been shown to exhibit a very good resistance to stress corrosion cracking and sea water corrosion\textsuperscript{36}. 
2.1.3 Sputtering:

Sputtering is very effective in preparing single phase alloys from elements whose melting points are greatly different from each other. In the cases of Al-Ta, Al-Nb, Al-Mo and Al-W alloys, the melting points of Ta, Nb, Mo, and W exceed the boiling point of Al. Consequently these alloys can not be prepared by conventional melting practices. Sputtering is also known to form amorphous structures over wide composition ranges of the alloys. It is also possible to obtain alloy films with a range of microstructures and compositions by selecting / controlling the operating variables such as sputtering gas, gas pressure, electrical and magnetic parameters, substrate characteristics and deposition temperature and choosing the appropriate sputtering apparatus. A number of supersaturated Al alloys with a range of alloying element concentrations were obtained by the co-sputtering methods\textsuperscript{25,39-51}. Other materials that will also be discussed under this category are stainless steel films and Fe alloy films.

2.1.3.1 Supersaturated Al alloys:

Thin Al alloy films containing dilute concentrations (0-10 at\%) of elements such as Cr, Mo, Ta, Zr, Cu, Si, V, Nb, W etc. were deposited on single crystal Si substrates in a RF magnetron Co-sputtering unit\textsuperscript{25,39-41}. The concentration of the alloying element is varied by independently varying the sputtering rate of Al and the alloying element targets. Frankel\textsuperscript{42} and Hashimoto\textsuperscript{43-51} used the same method to prepare Al alloys with higher concentration (10 - 60 at\%) of alloying elements. The substrates used in this study were aluminum disc or Pyrex plate or quartz plate. In all of the above investigations\textsuperscript{25,39-51}, the concentration of the
alloying element varied slightly across the thickness of the sputtered alloys reaching the highest concentration at the substrate / film interface. From X-ray diffraction studies\textsuperscript{44}, it was deduced that the solid solubility of all of the alloying elements in Al has been extended. Depending upon the alloying element concentration, either crystalline or amorphous or a mixture of amorphous and crystalline structures were obtained (Figure 9). The structures were predominantly crystalline, when the alloying element concentration is less than 10 at\%. Potentiodynamic polarization behavior of the dilute Al alloys were determined in deaerated and aerated neutral chloride solutions. The structure and composition of the passive films were determined by X-ray Absorption near Edge Structure (XANES)\textsuperscript{41} and X-ray Photoelectron Spectroscopy\textsuperscript{39}, respectively. Alloying elements such as Cr, Mo, Ta, and W significantly increases the pitting potential of Al even though the passive current densities of these alloys are similar. Highest pitting potentials were obtained for Al-W alloys, even though no oxidized species of W was observed in the passive film. The enhanced pitting performance of these alloys has been correlated to either enrichment of oxidized species of alloying elements in the passive film or to the structural modifications occurred in the passive film, i.e., to chloride ion penetration characteristics of passive films. On heating the sputtered alloys, the precipitation of second phases was observed. The corrosion resistance of the heat treated alloys rapidly deteriorated\textsuperscript{25}.

Hashimoto et al\textsuperscript{43-51} found that the corrosion rates of the Al alloys containing high concentrations of alloying elements in 1 M HCl at 30 C decreased with the alloying element concentration. Ta and Nb were more effective
Figure 9 Structure of sputter-deposited Al alloys identified by X-ray diffraction (ref. 44)
compared to other alloying elements in decreasing the corrosion rate. The pitting potentials of the Al alloys containing high concentrations of alloying elements were determined in 0.1 M NaCl solution at pH = 10\textsuperscript{42} and in 1 M HCl solution at pH\textsuperscript{=0}\textsuperscript{43-51}. At these high concentrations, Ta and Nb were again found to increase the pitting potential of Al more than the other alloying elements. Again, the localized corrosion resistance of the alloys have been correlated to the passive film characteristics such as thickness and the presence of oxidized species of alloying elements\textsuperscript{43-51}.

2.1.3.2 Stainless steels and Fe base alloys:

In the pursuit of obtaining amorphous materials with high corrosion resistance, stainless steel films were prepared by the sputter-deposition method. The substrates used were Al, stainless steel and Cu. The pitting potential of microcrystalline sputtered stainless steel films was 300\textsuperscript{52} and 500\textsuperscript{53} mv higher than that of the target material of the same composition. the microstructure of sputtered-deposited stainless steel films was evaluated as a function of the deposition temperature\textsuperscript{53,54,55} and annealing temperature\textsuperscript{56}. The structure of the film deposited at temperature below 375 C was determined to be body-centered cubic. Films deposited at higher temperatures exhibited either FCC or a mixture of BCC and FCC structures. Columnar grain microstructures with an average grain size of 2-2.5\(\mu\) were observed on the single phase (either BCC or FCC) stainless steel films. On the other hand, 0.7-1.5 \(\mu\) diameter equiaxed grains were found for the two phase deposits. Larger crystallites were obtained by higher annealing temperatures and longer annealing times\textsuperscript{56}. The high temperature oxidation resistance of the fine grained sputter-deposited stainless steel was
determined to be superior to that of coarse grained wrought material of the same composition\textsuperscript{57,58}. This improved scaling resistance was attributed to (i) enhancement of Cr diffusion at the grain boundaries; (ii) reduced stresses in the oxide; (iii) improved adhesion of the oxide; and (iv) stability of the grain size for the sputtered material.

Amorphous structures in stainless steel were obtained either by sputtering the films on the substrates maintained at liquid nitrogen temperatures\textsuperscript{59} or by the addition of alloying elements such as Al\textsuperscript{53}, Si\textsuperscript{53}, W\textsuperscript{60,61}, Ti\textsuperscript{61}, and Zr\textsuperscript{62}. Wang\textsuperscript{63} suggested that amorphous structures can also be obtained by adding appropriate amounts of elements such as Hf, Nb, Mo, Ta, etc. The localized corrosion resistance of these amorphous films\textsuperscript{53,60} was observed to be similar to that of the amorphous Fe-Cr alloys\textsuperscript{4-6,64-66} containing metalloid elements such as P, Si, C, or B. The pitting potentials of these alloys with amorphous structures were approximately 700-1000 mV higher than that of conventional 304 type stainless steel. The recrystallization temperature of the amorphous films was found to increase with the addition of refractory metals such as W and Ti. The corrosion resistance of 304 type stainless steels containing 11 to 53 % W was preserved even after the heat treatment at crystallization temperature\textsuperscript{61}.

2.1.4 Ion-beam surface modification methods:

Ion-beam techniques such as ion implantation, ion beam mixing, and ion beam assisted deposition (IBAD) can be used to modify metal surfaces with improved mechanical, electrical, optical, and electrochemical properties. In ion
implantation, the alloying element is ionized, accelerated to high energies and is
bombarded with the material to be implanted. In ion-mixing, a preformed surface
film or a sequence of multilayers obtained by deposition methods is completely
intermixed with the substrate by heavy ion bombardment to form an alloy or a
compound. If the deposition and the bombardment are carried out
simultaneously, then the method is referred as ion beam assisted deposition.
The accelerating voltage and the current density usually vary from 10-200 KeV
and from 0.1 to 4 \( \mu \text{A/cm}^2 \), respectively. The dose of the implanting species is
typically of the order of \( 10^{14} - 10^{18} /\text{cm}^2 \). Through ion beam techniques, the
corrosion processes can be altered by modifying either the anodic or cathodic
processes or the passive film or by producing corrosion resistant coatings such
as oxides, nitrides, etc.

2.1.4.1 Fe base alloys:

Earlier works on ion-implantation involved the irradiation of materials such
as carbon steels with gaseous ionic species such as He\(^+\), O\(^+\), Ar\(^+\), and N\(^+\).\(^{67,68}\)
N\(^+\) bombardment was found to be beneficial in significantly increasing the pit
initiation time in mild steel. Implantation of Cr\(^+\), Ti\(^+\), and Ta\(^+\) species\(^{69-72}\) in low
carbon steels that were carried out in the last decade indicated substantial
improvements in general and localized corrosion behavior. The critical current
density required for passivation and the passive current density were decreased
by two to three orders of magnitude. The IBAD procedure produced better quality
corrosion resistant coatings compared to those produced by deposition methods
alone. A reduction in porosity, increased adhesion and enhanced
microcrystallinity were observed in IBAD coatings.
Amorphous microstructures were obtained in the metal surfaces with the implantation of moderately high doses of ionized metalloid species such as P⁺, C⁺⁷³-⁷⁶, etc. The substrate materials used were stainless steels, Fe, Fe-30 at% Ni, and Fe-12 to 18 at% Cr alloys. By ion implantation, the concentration of the metalloids at surface and subsurface regions reached levels as high as 20-60 at%. Amorphous Fe-Cr-P alloys prepared by ion-beam mixing compared well to the metallic glasses prepared by rapid quenching in general and localized corrosion performance. However, the crystalline Fe-Cr-P alloys prepared by ion-mixing performed much better than the crystalline counterparts obtained by heat treating the rapidly solidified metallic glasses. According to Demaree et al⁷³, the presence of P present in ion mixed Fe-Cr-P alloys increased the amount of Cr in the passive film. This conclusion was the same as that reached by Hasimoto⁴.

2.1.4.2 Al base alloys:

Metastable Al alloys containing Mo, Si, Cr, Zr, Nb, Ta, and W⁷⁷-⁸¹ in the surface layers of Al were prepared by ion implantation, and in some cases by ion mixing and ion beam assisted deposition⁸² methods. The concentration of the implanted species was typically non-uniform reaching the peak value at the distances of about 300 Å from the surface. The total depth of penetration of implanted species is about 500 Å. Except Al-Zn and Al-Mg alloys, the metastable Al alloys were found to exhibit pitting resistance superior to Al. However, the passive current density of the alloys including Al-Zn and Al-Mg was similar. A correlation was observed between the pitting potential of the alloys and the pH of zero charge of the hydrated alloying element oxide(pHₐₓ). According to Natishan⁸⁰ et al, the chloride adsorption characteristics of the passive films were
the rate limiting step of the pitting process. An ion-beam mixed Mo film and IBAD Ta exhibited better corrosion resistance compared to Mo and Ta coatings, respectively, obtained by physical vapor deposition.

2.1.5 Electrodeposition and Electrolessdeposition:

Both electrodeposition and electrolessdeposition are easier, faster and more economical methods than sputtering and ion plating methods. Deposits up to several micrometers thick with a good adherence to substrates can be achieved. A wide range of alloy compositions can be obtained by varying the cathodic potential or cathode current density, electrolyte bath composition (including addition of complexing agents), etc. To be effective, the deposited alloys must contain a good film-forming element like Cr, Ti, or W. In the electrolessdeposition process, metallic coatings are produced by a chemical reduction process. Examples are the preparation of Ni, Co, and Pb films by reduction of their chlorides by sodium hypophosphite. Amorphous alloys produced by plating processes are listed in Table 1. Amorphous structures were obtained by the additions of high concentration of either metalloids or refractory metals, similar to the case of rapidly solidified glassy metals. The corrosion behavior of electrodeposited Fe-Cr-P alloy was comparable to the same alloy produced by either rapid solidification or ion mixing, when the concentration of Cr was sufficiently high (7 to 9 at%) .
### Table 1

**Amorphous and amorphous-like alloys deposited by plating methods (ref. 83)**

<table>
<thead>
<tr>
<th>Electro plating</th>
<th>Electroless plating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi - S</td>
<td>Ni - W</td>
</tr>
<tr>
<td>Bi - Se</td>
<td>Co - W</td>
</tr>
<tr>
<td>Cd - Te</td>
<td>Co - Re</td>
</tr>
<tr>
<td>Cd - S - Se</td>
<td>Co - V</td>
</tr>
<tr>
<td>Si</td>
<td>Fe - W</td>
</tr>
<tr>
<td>Si - C - F</td>
<td>Fe - Mo</td>
</tr>
<tr>
<td>Ni - P</td>
<td>Cr</td>
</tr>
<tr>
<td>Ni - S</td>
<td>Cr - W</td>
</tr>
<tr>
<td>Fe - P</td>
<td>Cr - Mo</td>
</tr>
<tr>
<td>Co - Ni - P</td>
<td>Cr - Fe</td>
</tr>
</tbody>
</table>
2.1.6 Laser surface processing:

Lasers with continuous outputs of 0.5 to 10 kW\textsuperscript{85} can be used to modify the composition and microstructure metal surfaces to tailor the surface properties without greatly effecting the bulk properties. The surface modification can be done by lasers in three ways. The first is transformation hardening in which the surface is heated so that controlled solid state transformations take place. The second is surface melting, which results in refinement of structure due to rapid quenching of the melt. The third is surface alloying, in which the alloying elements are added to the melt pool to change the composition of the metal surface. The electrochemical properties of metal surfaces can be modified by all of the three methods. The processing variables are laser power, power density, interaction time, atmosphere composition and rate of material addition. The laser treated surfaces are microcrystalline rather than glassy, because the cooling rates are not as high as required to suppress crystallization. The primary advantages of laser processing are (1) leveling of large scale variations in composition, (2) fine distribution of second phase precipitates and impurities, (3) a slight extension of solid state solubility limit, and (4) enrichment of passivity promoting elements like Cr in the surface layers of metals and alloys. A low uniform corrosion rate (\(< 1 \mu m / year\)) and a high pitting resistance in NaCl solution was achieved with laser alloyed Fe-Ni-Cr surface on mild steel\textsuperscript{86}. Even though the increase in the pitting potential was only marginal, a marked decrease in critical current density required for passivation and a reduction in the width of active/passive transition region were observed in laser processed 304 type stainless steel and ferritic Fe-13Cr-Mo(0 to 5\%) steels\textsuperscript{87}. Laser glazing has also
been used to make glassy surface layers of general composition Fe-Ni-Cr-P-B\textsuperscript{64}. The surface layers were found to consist of both crystalline and amorphous phases. The crystalline phase rapidly dissolved in 10% FeCl\textsubscript{3} solution. The amorphous phase was heavily cracked as a result of internal stresses created by laser glazing process. Even though the glass layer was found to be extremely resistant to FeCl\textsubscript{3} solution, severe pitting and crevice attack of substrate took place as a result of electrolyte penetration through the microcracks in the glassy layer. Recently, amorphous structures were found on the surface of the laser treated Mg-Zr alloys, when the Zr content is about 85 at%\textsuperscript{88}. It is suggested that the corrosion properties of Mg alloys can be significantly improved by laser alloying with higher concentrations of Zr.

2.2 Pitting mechanisms of metals and alloys:

Pitting corrosion is a complex phenomenon and is effected by a number of materials parameters and environmental variables. It demands the attention of many disciplines such as metallurgy, electrochemistry, physics, surface science and analytical chemistry. It is important to understand the fundamental processes involved in pitting in order to develop corrosion resistant materials and the most effective corrosion protection methods.

The development of a corrosion pit can be thought of as occurring in several stages. Stage 0 assumes the presence of a protective film covering an otherwise reactive metal; stage 1 represents the occurrence of a localized breakdown of passive film; stage 2 involves the early development of a solution chemistry different from the bulk within the restricted region of the film that
underwent breakdown; stage 3 represents the widening of the pit to a size greater than atomic dimensions with the development of new chemistry and / or an occluded cell situation; In stage 4, the pit has grown to millimeter dimensions and represents a threat to the integrity of the structure. Different approaches were followed by various researchers to investigate pitting, depending on their interests and expertise. Accordingly, a number of pitting models have been proposed. In essence, the rate limiting step in the stable pitting process was either associated with the breakdown of the passive film (or pit initiation) or the establishment of pit chemistry that prevents the repassivation process. Based on these criteria, the pitting models can be classified into two categories: (a) Models taking into consideration both pit nucleation and pit growth; (b) Models taking into consideration only pit growth (example: localized acidification theory).

The existing pit nucleation models can be divided into two groups. In the first group, pits nucleate at the metal / oxide interface and the metal is primarily attacked. In the second case, pits initiate at oxide / electrolyte interface and the oxide film suffers dissolution starting from the outermost layer. In both groups, the adsorption of aggressive species is considered as the first step to pitting process. The proposed models belonging to these groups are listed as follows.

Group I: (a) Anion Penetration/Migration Models
(b) Point Defect Model
(c) Mechanical Breakdown Models
(d) Percolation Model
In these models, it is assumed that the passive films contain flaws, pores, or other physical defects and a direct reaction will occur between the metal and the aggressive species.

**Group II: Chemical Dissolution Models**

These models involve the attack of the passive films by halogen ions through one of the following phenomena: (i) formation of chloride complexes due to direct reactions of hydrated oxide film with chloride ions; (2) formation of salt nuclei as a result of reaction of metal cations and the aggressive anions; (3) and replacement of oxide ions in the oxide lattice by chloride ions.

A critical review of all of the pit initiation models has been performed by Smialowska. In all of the models, the passive film properties play an important role in either breakdown / pit initiation process. Also, the pitting resistance of a number of metals and alloys has been correlated to the protective quality of the passive film. Some of the passive film characteristics that affect the pit initiation process and the pitting resistance are discussed below.

**2.2.1 Passive film characteristics that affect pit initiation and pitting resistance**

**2.2.1.1 Anion adsorption characteristics:**

It is generally accepted that the adsorption of the chloride ions is the first step of several events that lead to pitting. The Cl\textsuperscript{−} adsorption measurements performed by Yovancicevic\textsuperscript{90} et al on passive iron showed that Temkin's
isotherm is obeyed. The metal surface was found to be inhomogeneous, consisting of a number of defects, and the adsorption energy varied from site to site. Accordingly, the adsorption of chloride ions was determined to be localized. Analytical techniques such as Autoradiography, Secondary Ion Mass Spectroscopy (SIMS), and X-ray Photoelectron Spectroscopy revealed the adsorption of Cl\(^-\) ions also on passive films on Al at open circuit potentials as well as anodic potentials. Berzing measured the adsorption isotherms on corroding Al with Cl\(^-\) and concluded that chloride adsorption was primarily localized to the corroding pit sites. The adsorption of chloride ions on the passive films on Fe as well as Al was found to increase linearly with the potential.

2.2.1.2 Film structure and composition:

The structural characteristics that were found to influence the pitting process are (a) crystal structure, (b) the degree of non-crystallinity of the oxide film, (3) size, shape and distribution of micro as well as macro defects. All these characteristics were found to depend on the material composition, anodic potential, electrolyte composition and the temperature. Air-born oxide on Al was observed to be amorphous, whereas, the structure of the oxide obtained by thermal oxidation of Al was strongly dependent on the temperature. Anodic films that were grown in borate and tartaric acid solutions on Al are thin, dense, coherent and amorphous, whereas the films grown in sulfuric and phosphoric acids contain layers that are thick, porous and crystalline. The increased absorption of Cl\(^-\) ions observed by several authors at high temperatures may well be due to increased porosity of the passive film.
Reflected Extended X-ray Absorption Fine Structure (reflEXAFS)\textsuperscript{41} studies revealed that the structure of passive film on Al - Mo alloys is $\alpha$-Al$_2$O$_3$, whereas, the structure of the oxide film on Al is more closely related to $\gamma$-Al$_2$O$_3$. It was suggested by Davis et al\textsuperscript{41} that $\alpha$-Al$_2$O$_3$ is more resistant to chloride ion penetration increasing the pitting resistance of Al - Mo alloys. The structure of passive films formed on Fe-Cr alloys was investigated by McBee and Kruger\textsuperscript{95,96} from electron diffraction methods. Crystalline passive films were observed on the alloys containing less than 12 at\%%. The increase in the pitting potential of Fe-Cr alloys for Cr contents $>$ 12 at\% was correlated to the non-crystalline nature of the passive film. Localized corrosion in pure metals is primarily determined by the presence of physical defects such as slip steps, vacancies, pile ups, grain boundaries, and dislocation networks present on the metal surface. Harayuma\textsuperscript{97}, Doehing and Heusler\textsuperscript{98} argued that the pits in pure iron would form only when dislocations are present. However, several engineering materials contain second phase precipitates and inclusions, which further increase the defect density in the passive films. Microcrevices may also form between the metal matrix and the inclusions. The variation of chemical and physical defects from one region to another region lead to significant variations in the measured values of pitting potential and induction time. Shibata and Takayama\textsuperscript{99,100} proposed statistical pitting models (These models are discussed in detail in section 2.2.4, page 63) to describe those variations quantitatively. They were able to explain the abnormal distribution of the induction time found for numerous samples by assuming that pitting is a combination of pit formation and repassivation occurring simultaneously. The pitting survival probability decreased with corrosion time.
The composition of passive films on Fe base alloys, stainless steels, and Al alloys has been determined by a number of surface analytical techniques such as X-ray Photoelectron Spectroscopy (XPS), Auger Electron Spectroscopy (AES), UPS, Ion Scattering Spectroscopy (ISS), Infrared (IR) and Raman Spectroscopy, and Secondary Ion Mass Spectroscopy (SIMS). It was found by XPS \(^{101,102}\) studies that the oxidized Cr content in the passive film on Fe-Cr alloys increased significantly, when the Cr content in the alloys is increased beyond 13 at%. The high corrosion resistance of Cr rich Fe-Cr alloys and stainless steels was attributed to the protective nature of chromium hydroxide present in the passive films. Recently, the composition of passive films on a series of metastable sputtered Al alloys has been evaluated from XPS measurements by Davis et al \(^{103,104}\) and Hashimoto et al \(^{13,43,45,47}\) in neutral and acidic solutions, respectively. Davis et al reported that the passive films contain 5 - 10 at% of oxidized solute in the case of Al - Mo, Al-Cr, Al-Zr, and Al-Ta alloys. Only one oxidized form of the solute, i.e. Ta\(_2\)O\(_5\) or ZrO\(_2\) was found in Al-Ta and Al-Zr alloys, respectively. In contrast, up to three different oxidized states were present in Al-Mo and Al-Cr. It was also observed that the concentration of the oxidized solute in the passive film depended strongly on the anodic potential, increasing approximately five fold from the corrosion potential to the pitting potential. Figure 10 shows the ratio of oxidized Ta or Cr to Al, as a function of overpotential for Al-Cr and Al-Ta alloys. Davis et al proposed that the enhanced passivity achieved in these alloy systems was due to the hindrance offered by the oxidized solutes such as MoO\(_4\)\(^{2-}\), CrOOH, and Ta\(_2\)O\(_5\) to chloride ion penetration. In a separate study, Gonzales-Martin et al \(^{105}\) observed the enrichment of Ta species in the
Figure 10  Ratio of oxidized alloying element to oxidized Al as a function of overpotential for Al-Cr and Al-Ta alloys in deaerated 0.1 M KCl (ref. 103)
passive films formed in 0.1 M NaCl solution on Al-Ta alloys. According to Gonzales-Martin et al.\textsuperscript{105}, the presence of Ta species slowed down the dissolution process of Al by blocking paths used by chloride ions to reach the oxide / metal interface, and by means of the fact that Al-Ta bonds are stronger than Al-Al bonds. In the case of Al-W alloys, only a small amount of oxidized W (WO$_3$ and WO$_2$) was found at high anodic potentials, even though the Al-W alloys exhibited the highest pitting potentials (approximately 1400-2000 mV higher than that of Al). Hashimoto et al.\textsuperscript{13,43,45,47} also observed the enrichment of the oxidized Mo, W, Nb, Ta, and Zr in the passive films grown on the corresponding binary Al alloys in 1 M HCl. Figure 11 shows the enrichment of Ta as a function of overpotential in Al-22 at% Ta alloy. The concentration of the oxidized solutes increased initially at lower anodic potentials, but remained constant on further increase with the potential till the pitting potential is reached. Again, the high pitting resistance of the alloys has been correlated to the passive film chemistry (enrichment of oxidized alloying elements) similar to the proposition made by Davis et al.

Passive films formed on stainless steels, sputter-deposited Al film, metastable Al-Cr, Al-Mo, Al-Ta, and Al-W alloys were found to contain water molecules. The effect of incorporated water on the pitting susceptibility of stainless steel was studied by Okamoto\textsuperscript{106} and his coworkers. Hydrated oxide films were believed to be more resistant to breakdown and pitting because of their good repairing action provided by the abundance of water molecules. However, no repairing of the film occurs if the chloride ions penetrated the passive film. Pou et al.\textsuperscript{89} observed that the chloride ions replaced water
Figure 11  Cationic fractions in the surface film formed on the Al-22 at%Ta alloy (ref. 43)
molecules at breakdown potentials and at high temperatures. AES and XPS techniques revealed the presence of chloride ions in the passive films formed on iron\textsuperscript{107}, iron base alloys\textsuperscript{108}, and Al\textsuperscript{109}. Most of the results indicated that the chloride ions exist only in the outer layer of the film. The outer layer formed as a result of the transfer of metal ions to the solution primarily consists of precipitates such as oxyhydroxides and chloride salts.

The protective quality of passive films formed on certain alloys has been linked either to the acidic / basic character\textsuperscript{110} or to a modification of defect chemistry\textsuperscript{111} of the passive films. Addition of alloying elements such as Al, Sn, Mo, and Si (which form acidic or amphoteric oxides) extended the passivity of parent metals such as Fe, Ni, Cu, Cd, and Hg (which form basic oxides) over a wide range of pH's and potentials. According to Hoar\textsuperscript{110}, a strong interaction between the acidic oxides of alloying elements and the more easily dissolved 'basic' oxides exist resulting in the formation of salt-like oxides. Since the solubility of salt-like oxides formed on the alloys is considerably lower than that of basic oxides, the passive films formed on the alloys are relatively more stable. MacDonald\textsuperscript{111} proposed that the enhanced pitting resistance of Fe-Cr alloys obtained by the W and Mo additions was due to the formation of complexes between the mobile cation vacancies and the immobile, highly charged W\textsuperscript{6+} and Mo\textsuperscript{6+} ions. Since the flux of the cations is reduced by the decrease in the cation vacancies (formation of complexes involves a consumption of cation vacancies) as well as a decrease in their mobility, a higher anodic potential or a longer induction time is necessary to establish the build up of a critical concentration of cation vacancies at metal / oxide interface to cause pit nucleation.
2.2.1.3 Effect of passivating conditions:

The breakdown susceptibility of passive films also depend on the film history, for example, the time of introduction of the aggressive anions in relation to the passivation process. Pitting of iron was observed in a NaOH solution (pH=12) containing chloride ions. However, the same specimen resisted pitting when the chloride ions are added after the passivation\textsuperscript{112}. Similarly, iron did not undergo pitting in a borate solution of pH=10.4, if chloride ions were not added before iron passivated\textsuperscript{113}.

Oxide films grown on metals in various solutions and under different experimental conditions showed significant differences in quality. This is either due to the incorporation of different anions or to the reduction of oxides taking part in film formation\textsuperscript{114,115}. Some of the inorganic anions incorporated in the film showed beneficial general and localized corrosion properties. AES and Ellipsometric investigations\textsuperscript{116} showed that the passive films on Fe consist of two layers, when anions such as $\text{SO}_4^{2-}$ or $\text{PO}_4^{3-}$ were incorporated in the film. The concentration of passivating electrolyte, for example, borate solution has a significant effect on the thickness of the passive film\textsuperscript{117}.

2.2.1.4 Film thickness:

The effect of film thickness on pitting susceptibility was studied by many authors, but the conclusions are contradictory. In some cases, the induction time for pitting increased with film thickness, and in others such a dependence was not observed. Generally, passive films formed on Cr rich Fe-Cr alloys and
stainless steels are thinner and more protective than those formed on iron and iron-carbon alloys. Similarly, the barrier oxide films formed on Al were thinner and more resistant to chloride ion penetration, compared to the thicker porous oxide films. However, Hashimoto et al.\textsuperscript{13,43,45,47} observed that the passive films formed on several sputtered Al alloys in acidic chloride solutions are thicker at pitting potentials, but more protective than those formed on Al. The thickness of surface film formed on amorphous Al-Ta alloys is shown in Figure 12. The pit density of iron was found to decrease with the thickness of the air-formed oxide films grown below 200 C (obeyed logarithmic kinetics), but was independent of the film thickness for films grown above 250 C (obeyed parabolic kinetics).\textsuperscript{118}

2.2.1.5 Semiconducting properties and photoeffects:

The oxide films grown in aqueous environments on a majority of metals and alloys display semiconductive properties. The semiconductive properties of the passive films were observed to vary with environmental and material variables and exhibited a correlation with the susceptibility of pitting. Depending upon the heat treatment, the passive films on stainless steels exhibited either p-type or n-type. The conductivity of the passive films on stainless steels also changed from p-type to n-type after a prolonged exposure to the boiling solutions of MgCl\textsubscript{2}, NaCl and CaCl\textsubscript{2}.\textsuperscript{119} This change was attributed to a modification of density and type of defects. At higher electrolyte temperatures, the oxide films on 304 type stainless steel behaved predominantly as n-type semiconductors.\textsuperscript{120} When higher anodic voltages are applied, the space charge region can be inverted to p-type for a n-type conductor, and to n-type for a p-type
Figure 12  Thickness of surface films formed on amorphous Al-Ta alloys in 1 M HCl (ref. 43)
semiconductor. The number of pits was greater when the films were of the n-type than in cases of p-type.

The photoeffects can be easily related to the semiconducting nature of the passive film. The concentration of carriers near the surface can be increased by illumination. MacDonald et al found a significant decrease in the number of pits and an increase in the breakdown potential, when nickel oxide (p-type semiconductor) was illuminated in comparison to the case of dark conditions.

2.2.2 Pit Initiation models:

2.2.2.1 Adsorption models:

Uhlig stated that pits were formed as a result of the competitive adsorption of chloride ions and oxygen. According to this concept, the pitting potential \( E_{np} \) is the potential at which the adsorbed anionic species displace the adsorbed passivating species such as water or oxygen ions on the metal surface.

When a passivated metal is immersed in water, a 'hydrated' surface layer forms as a result of adsorption and interaction of water with the oxide film. The surface charge and, hence, the adsorption characteristics of the passive films was found to be controlled by the pH of zero charge of hydrated oxide. The pH of zero charge of an oxide, \( pH_{ZCH} \), is the pH at which the concentration of OH\(^-\) and H\(^+\) ions are equal, i.e., the oxide surface has no net charge. At pH's higher than the \( pH_{ZCH} \), the oxide surface is negatively charged and the chloride adsorption does not occur. At pH's lower than the \( pH_{ZCH} \), the surface conditions
are highly in favor of adsorption of chloride and other anions. The predominant
process of adsorption in pitting phenomenon is very evident when the pitting
potentials of pure metals are plotted against the pH\textsubscript{ZCH} of the hydrated oxide of
the corresponding element (Figure 13)\textsuperscript{80}. The pitting potential increases
significantly with a decrease in pH\textsubscript{ZCH}. The pH\textsubscript{ZCH} argument has been extended
later by Natishan and McCafferty to account for the high pitting resistance of ion-
beam processed Al alloys. Alloying elements such as W, Mo, Si, Cr, Zr, and Nb
for which the hydrated oxides have a pH\textsubscript{ZCH} lower than that of hydrated
aluminum oxide increased the pitting potential of Al, whereas implantation of Zn
for which the hydrated oxide has a higher pH\textsubscript{ZCH} than hydrated aluminum oxide
decreased the pitting potential of Al (Figure 14)\textsuperscript{77}.

2.2.2.2 Anion penetration / migration models:

As early as 1927, Evans\textsuperscript{125} suggested that chloride ions can penetrate the
protective oxide film because of the smaller size (ionic radius = 1.81 Å). In 1965,
Hoar\textsuperscript{126} suggested that pit initiation is caused by the penetration of chloride
anions under the influence of an electrostatic field. The breakdown potential will
correspond to a potential at which a critical value of the electric field is reached.
According to this model, Cl\textsuperscript{−} ions are more aggressive than Br\textsuperscript{−} and I\textsuperscript{−}
because of their smaller size. Rosenfeld and Marshakov\textsuperscript{127} suggested in 1964 that chloride
ions can displace oxygen ions in the oxide lattice, penetrate the passive film and
agglomerate inside the pit. Pits are therefore equivalent to closed crevices
covered by a porous membrane. In this case, the geometric factors control the pit
initiation similar to crevice corrosion. McBee and Kruger\textsuperscript{128} assumed in 1974 that
anion vacancies are created during the migration of chloride ions.
Figure 13  Pitting potentials of oxide covered metals vs. the pH of the oxides (ref. 80)
Figure 14  Pitting potentials of ion implanted and sputtered Al alloys as a function of pH$_{zch}$ (ref. 25, 39-41, 42, 80)
It was suggested that chloride ions exchange with oxide and hydroxide ions according to the following equation.

\[
\text{Cl}^{\text{soln}} + O^{2-} + 2 \text{OH}^{\text{lattice}} \rightarrow \text{Cl}^{\text{lattice}} + 2 \text{OH}^- + 2\text{OH}^{\text{soln}} \tag{1}
\]

In this model, the induction time is considered as the time needed for anion migration through discrete defects to reach the bare metal. The pitting potential is the potential at which the damaging anions are adsorbed on the passive film. According to Yovancicevic et al.\(^{90}\), the passive film on Fe underwent breakdown when the total concentration of adsorbed and absorbed chloride ions reached a critical factor of 1.3. The higher the bulk concentration of chlorides, the lower the breakdown potential.

The anion penetration model is supported by (a) a direct relationship experimentally observed between the induction time and the thickness of the film existing on iron and (2) the presence of chloride ions detected by refEXAFS technique\(^{129}\) in the passive films on Fe and Fe-Cr (14 and 24 at% Cr) alloys. Hashimoto et al.\(^ {13,43,45,47}\) and Davis et al.\(^ {103,104}\) found the enrichment of oxidized alloying elements such as Cr, Mo, Ta, Zr, and Nb at anodic potentials in the passive films formed on supersaturated Al alloys and proposed that these alloying element oxidized species inhibit the penetration of chloride ions. However, the following observations contradict the anion penetration model.

(i) The majority of the XPS and AES studies of oxide films grown on Fe, steel, and Al indicate that the chloride ions exist only at the outer layer of the films, and are not incorporated throughout the film\(^ {89}\).
(ii) pitting by anionic species such as $\text{SO}_4^{2-}$ and $\text{ClO}_4^-$ with larger ionic radius cannot be explained.

(iii) The pH dependence of the pitting potential of Fe observed in a borate solution (pH=8.45) containing chloride ions cannot be explained$^{130}$.

(iv) The nucleation of pits in Ni under certain conditions is so fast$^{131}$, it cannot be explained by anion migration model.

2.2.2.3 Point Defect Model:

Lin$^{132-134}$, Chao$^{132-134}$, and MacDonald$^{132-134,135}$ attributed breakdown or pit initiation to the pile up of 'metal holes' (cation vacancies) at the metal / film interface during the passive film growth process. This collection of 'metal holes' results in a growing void at the metal / film interface which causes the passive film to suffer a local collapse when the void reaches a critical size at the end of the induction period. Film breakdown is assumed to occur both in the presence and the absence of the halogen ions, but greatly accelerated in the former case. It was assumed$^{135}$ that initial event that occurs at the barrier layer/environment interface in passivity breakdown is the absorption of aggressive ions such as chloride ions into a surface oxygen vacancy.

$$ V_{\text{O}}^{\text{v}} + \text{Cl}^- = \text{Cl}^\prime \text{O} \quad -------- \ (2a) $$

or

$$ V_{\text{O}}^{\text{v}} + \text{Cl}^- . n\text{H}_2\text{O} = \text{Cl}^\prime \text{O} + n\text{H}_2\text{O} \quad -------- \ (2b) $$
followed by a Schottky-pair type reaction

$$\text{Null} = \text{VM}_M^{x'} + \frac{x}{2} \text{VO}^-$$  \hspace{1cm} \text{(3)}

which leads to the generation of cation vacancies at the film/solution interface and hence to the increased flux of cation vacancies across the barrier layer. The Gibbs free energy, hence the reaction rate for the reaction (2b), depends on the dehydration energy of the hydrated chloride ions as well as the energy required to expand the vacancy to accommodate the chloride ion. The semi-quantitative calculations indicated that the chloride ion has the most favorable Gibbs free energy of absorption into an oxygen vacancy. In this model, the rate limiting step is the process of local agglomeration of cation vacancies leading to the film breakdown. Using this model, MacDonald and his coworkers were able to develop equations for the induction time and the critical breakdown potential that were in quantitative agreement with experimental data for the pitting of iron and nickel in halide containing solutions. This model also predicts that the metals exhibiting low cation vacancy diffusivities such as Ti, Ta, and Zr are quite resistant to pitting. Also, the dependence of the pitting potential on chloride ion concentration and the high pitting resistance of Fe-Cr alloys containing W and Mo were successfully explained by this model. The cumulative probability of the breakdown voltage obtained from this model fits very well to the experimental data obtained by Shibata for the pitting of Fe-17 Cr alloys in chloride solutions. Also, the photo inhibition of passivity breakdown can also be explained by this model. The photo-generation of electron hole pairs within the film reduces
the electric field and thus reduces the pit nucleation rate. However the following counter arguments can be made against this model.

(i) The non-uniform distribution of point defects, as assumed in this model, was not verified experimentally. It was assumed in this model that the growth of passive film occurs by anion transport at the metal / oxide interface. This is certainly true for valve metals such as Al, Zr, Ta, etc.; however extending the assumption to Fe and Ni, for which the model is successfully applied, is debatable.

(ii) Again, the pH dependence of the pitting potential cannot be accounted for by this model.

2.2.2.4 Mechanical breakdown models:

Hoar in 1947\textsuperscript{138,139} assumed that passive films in contact with aggressive solutions were mechanically stressed and damaged by pores and flaws. Aggressive anions were also assumed to replace water and reduce the interfacial tension (or interfacial energy) of the oxide / solution interface. Eventually, the interfacial tension is lowered so far that a peptization by interfacial charge occurs. The repulsive forces existing between the adsorbed anions detach the oxide film. Any crack or opening thus produced results in adsorption of additional anions on both sides, and the entire process becomes progressive. Richardson and Wood\textsuperscript{140,141} observed the internal flaws existing in passive films on Al by Transmission Electron Microscopy(TEM). Pits were presumed to propagate at these flaws. These authors considered the induction time as a stage during which the pits are too small to be visible and the current is too low to have a
measurable effect. Kruger\textsuperscript{142} suggested that pitting potential would become the potential for the adsorption of aggressive anions on the bare metal at the base of the pores. The incorporation of chloride ions and the increased pitting susceptibility of metals at high temperature were attributed to the thicker passive films, since thicker films are stressed more and can be broken easily. Sato\textsuperscript{143} suggested that the passivity breakdown occurs as the film attains a certain value of thickness, at which the critical mechanical stress is reached as a result of electrostrictional and electro-capillary forces. According to this concept, $E_{\text{np}}$ becomes the potential above which the electrostrictional forces exceed the compressive stress for film breakdown. The electrochemical measurements performed by Strehblow\textsuperscript{131} on Fe and Ni support this model. When sudden potential changes are applied to iron and nickel specimens, the nucleation of pits is so fast that it can only be attributed to mechanical breakdown of the film. Even when electrode potential is decreased in the negative direction, a large nucleation rate is observed. This observation can not be rationalized by any other model except the mechanical breakdown model. Similar to other proposed models, the existing mechanical breakdown models so far have not been supported by satisfactory experimental evidence in the majority of cases. Hoar's views\textsuperscript{138,139} are also not consistent with the observation\textsuperscript{130} that the breakdown rate varies linearly with chloride concentration. At higher chloride concentrations, the adsorption isotherm is generally observed to be non-linear. Hence, the surface tension (which is related to surface adsorption) would no longer vary linearly with chloride concentration and a linear breakdown rate (as is experimentally observed) would not be expected from the mechanical breakdown model. Also, there are no measurements of stresses in the passive films on
metals passivated in aqueous environments. Therefore, the question of whether
the mechanical breakdown of passive films can or cannot be the rate limiting step
in the pitting process is still open.

2.2.2.5 Percolation models:

Newman\textsuperscript{144-148}, Sieradzki\textsuperscript{144-147}, Song\textsuperscript{146,147}, and D. E. Williams et al\textsuperscript{148}
proposed percolation models of passivity to explain the passivity breakdown of
Fe-Cr alloys and stainless steels. A binary alloy with a square lattice (cubic
lattices in 3-dimensions) of randomly distributed Fe and Cr atoms can exhibit
passivity, when the concentration of Cr in the Fe-Cr alloys above the percolation
limit. The percolation limit is reached at a critical concentration of Cr above which
a connected path of Fe atoms cannot exist through the lattice.

Initially (for example, at open circuit potential conditions), in a two
dimensional lattice, Fe clusters are present at the surface as well as below the
surface. During passivation, Fe clusters at the surface are removed resulting in a
ramified interface of the alloy. Passivity arises, when the ramified interface
completely consists of Cr atoms. At this stage, the authors\textsuperscript{144-147} assumed a
small dissolution rate of Cr atoms (10\textsuperscript{-4} times lower than that of Fe). Progressive
dissolution of Cr atoms then uncovers iron clusters which subsequently dissolve,
causing current pulses; the charge distribution of the pulses thus reflects the
cluster size distribution. In particular, very large clusters are very rare. Iron
dissolution results in convoluted local penetrations of the lattice. It is proposed
that oxidation of the large number of surface Cr atoms within the convoluted
cluster region would acidify the local volume and so could lead, if the cluster is
large enough, to the establishment of the critical chemistry necessary for the activation of the alloy. The salient points are that pit nucleation is expected to be a rare event, because of the rarity of large iron clusters and that the pit generation should be proportional to the passive-current density. The passive current density as well as the distribution of Fe clusters are determined by the concentration of Cr in the alloy. According to these concepts, the passive film whose characteristics are measured by volume averaging techniques such as XPS, AES, EXAFS and SIMS is in fact the highly convoluted interface region and the film therefore appears to such techniques either as a non-stoichiometric oxide or a bilayer structure or a layer with short or long range order that is varying as a function of thickness or an entity incorporated with water and aggressive anions. It was interpreted from surface analytical instruments such as XPS and EXAFS that the passive oxide on stainless steels with low Cr contents contain hydrated oxides. According to this model, the hydrated layer is a part of a more convoluted interface expected at low Cr contents.

2.2.2.6 Chemical Dissolution Models:

All models belonging to this category assume that metal dissolution occurs by transient complex formation. Hoar and Jacob formulated the chemical dissolution theory after experimentally observing a slope of 2.5 to 4.5 between log $\tau$ (\(\tau\) = induction time) and log $Cl^-$ ($Cl^- = chloride concentration$) in pitting of austenitic steel. According to this theory, three or four halide ions jointly 'adsorb' on the oxide film around a cation preferably next to an anion vacancy. The transitional complex thus formed will be of high energy and the probability of its
formation at any instant will be very small. However, once formed, the complex can readily separate from the oxide lattice and dissolve in the solution quicker than the non- and aquo-complexed cations that are present in the film surface in the absence of halide solution. Under an anodic potential (positive electric field), a cation arrives at the oxide/solution interface to replace the dissolved cation. As a result of the above two steps, the electric field increases at a ‘thinned’ portion of the film at constant potential. As a result of the increase in electric field, more halogen ions are adsorbed on the oxide film and are attached to the cations. Therefore, once this ‘catalytic’ process has begun, it has a strong probability of repeating itself and accelerating because of the increased electric field. Thus, once the localized breakdown starts with a transitional complex, it accelerates rapidly. Heusler and Fischer¹⁵³ assume that chloride ions are inhomogeneously chemisorbed onto the passive film on iron in the form of two-dimensional islands that catalyze the oxide dissolution. Okada¹⁵⁴ proposed another model in which pits nucleate at solution/oxide interface. According to this proposition, cations diffuse through the film to the metal surface, reacting with halogen ions. As a result, salt nuclei are formed and grow inward. When these nuclei are stable and grow continuously, the salt nuclei permeate the passive film and dissolution of the metal occurs through the salt film. According to Foroulis and Thubrikar¹⁵⁵, the chloride ions adsorb at the oxide/solution interface in competition with OH⁻ or H₂O molecules under the influence of an electric field and react with the hydrated oxide surface to form a basic salt. Nguyen and Foley¹⁵⁶,¹⁵⁷ found that α-Al₂O₃ powder dissolves (40-60 µg per 10 g of powder) in neutral NaCl solutions (0.1 to 1.0 M NaCl). The greater solubility of aluminum oxide in fluoride solutions compared to the chloride solution of the same concentration was
attributed to the formation of a series of complexes ranging from $\text{AlF}^+$ to $\text{AlF}_6^{3-}$\(^{(158)}\). However, the chemical dissolution model was found not to be applicable in the following cases. For iron in borate solutions, the slope of log $t$ vs. log $\text{Cl}^-$ was found to be unity\(^{130}\), which can be interpreted either by the penetration or by the point defect model. The general breakdown of passivity of Fe, Ni\(^{159}\) in fluoride solutions starting from the pits suggested that in the presence of chloride ions the thinning of the passive films can occur at potentials lower than the pitting potential. Experiments conducted on Fe in alkaline solutions containing chloride solutions suggest that the thickness of passive films is greater at potentials closer to the pitting potential contradicting the thinning model\(^{160,161}\). The experimental results obtained for Fe in acidic and alkaline solutions suggested that either the mechanism of pitting in acids is different from that in alkaline solutions, or thinning of the film is not a determining step in pitting\(^{89}\). It is also difficult to conceive of thinning of oxide films as a decisive step in pitting of alloys like stainless steels which form highly resistant surface films.

### 2.2.3. Localized Acidification Theories:

As early as 1937, Hoar\(^{162}\) proposed a mechanism of 'autocatalytic' pit propagation as a result of pH drop inside the pit. In this proposition, the acidification was a result of the hydrolysis of corrosion products. It is now generally accepted that a low pH of the pit solution is one of the critical factors in stable pitting. Galvele\(^{163,164}\) developed a detailed local acidification model by assuming that flaws, cracks or micropits exist on the metal surface even below the pitting potential. The metal ions hydrolyze in these micropits or cracks and
the corrosion products are transported by diffusion. The important features of the unidirectional model suggested by Galvele, are the following:

(i) The metal dissolves only at the bottom of the pit, according to the general reaction

\[ M = M^{n+} + n \, e^- \] 

(ii) The reaction (2) is assumed to occur in non-complexing salt solutions. The pH of the bulk solution can take any value.

(iii) The metal ions are assumed to undergo hydrolysis by the following equilibria.

\[ M^{n+} + H_2O = M(\text{OH})^{(n-1)+} + H^+ \] 

\[ M(\text{OH})^{(n-1)+} + H_2O = M(\text{OH})^{(n-2)+} + H^+ \] 

\[ M(\text{OH})^{2+}_{n-2} + H_2O = M(\text{OH})^{+}_{n-1} + H^+ \] 

\[ M(\text{OH})^{+}_{n-1} + H_2O = M(\text{OH})_{n(aq)} + H^+ \] 

\[ M(\text{OH})_{n(aq)} = M(\text{OH})_{n(s)} \]
Reactions of this type are extremely rapid and the equilibrium (steady state) conditions were reached in a few μs. If the bulk electrolyte is alkaline, reaction (3) can be rewritten as

\[ 2 \text{M}^{n+} + \text{H}_2\text{O} + \text{OH}^- = 2 \text{M(OH)}^{(n-1)^+} + \text{H}^+ \]  

\[(6)\]

(iv) It is assumed that the aggressive salt anion acts as a supporting electrolyte for the ionic species formed by reactions (4) and (5). Now the transport equations are considerably simplified and only transport by diffusion becomes important.

From the equilibrium hydrolysis constants, the ionic product of water, the diffusivity values of various species and the proper flux equations set up for each type of atomic species (M, O, and H), the concentration of ionic and other soluble species can be determined as a function of the pit depth, x, and the current density in the pit, i. The detailed mathematical treatment was given in the papers (163,164). The concentrations of the soluble and precipitated phases as a function of x.i (product of x and i) in a unidirectional pit for iron in pH=10 solution are shown in Figure 15. The hydrogen concentration increases considerably during the pit growth. However, the solid Fe(OH)\(_2\) (the corrosion product that is formed as a result of hydrolysis inside the pit) is stable until x.i = 5 \times 10^{-7} \ A/cm and will lead to pit repassivation. Beyond this value, the proportion of solid phase drops sharply, and soluble products are mainly formed. At this stage, the conditions highly favor pitting. Therefore, the critical x.i value required for pitting can be based on the relative proportion of solid hydroxides and not on arbitrary critical acidification, as suggested in the earlier paper 163. Under stable pitting conditions, the current density inside the pits is of the order of 1 A/cm\(^2\). At this
Figure 15 Concentration of Fe$^{2+}$, FeOH$^+$, Fe(OH)$_2$(aq), Fe(OH)$_2$(s)
and H$^+$ as a function of the product of the pit depth ($x$) and the pit current density ($i$) (ref. 164)
current density, a diffusion path (micropit) of 50 Å (5 x 10^{-7} cm) is sufficient to reach the critical x.i value. The current density inside the micropit is a strong function of the anodic potential. This anodic potential should be high to generate a current density required for stable pitting. According to Galvele\(^{164}\) the pitting potential is the potential at which the critical value of x.i is reached. If the diffusion path is longer, as is the case in a crevice, lower current densities (hence, lower anodic potentials) are required to reach the critical value. Accordingly, crevice corrosion will start at a potential lower than that for pitting corrosion. Similarly, the pitting potentials of the samples with larger micropits will be lower than those with smaller micropits.

The critical value of x.i required for stable pitting of a number of divalent and trivalent metals and its dependence on the pH of the bulk electrolyte was also determined by Galvele\(^{164}\). The critical values of x.i are observed to be different for different metals. For divalent metals such as Fe, Ni, Co, Cd, and Zn, the critical value of x.i increased by one order of magnitude for each unit increment in pH, provided the bulk pH is above 10. For trivalent metal ions, like aluminum, the critical x.i value and hence the pitting potential is independent of the pH over a wide range.

According to the localized acidification mechanism, the pitting potential (\(E_{np}\)) has no thermodynamic meaning and is given by the following equation.

\[
E_{np} = E_{ca} + \eta + \phi + E_{inh} \tag{7}
\]
where $E_{ca}$ is the corrosion potential of the metal in the acidified pit-like solution, $\eta$ is the positive polarization voltage necessary to draw enough current through the pit to reach the critical $x.i$ value in the absence of inhibitors, $E_{inh}$ is the extra polarization required when inhibitors are present, and $\phi$ is the electric potential inside the pit when electric migration was taken into account. The experimental pitting potentials of Al, Al-3 at% Zn, and Fe-18Cr-xMo ($x = 0$ to $4.75$ at% ) alloys and those pitting potentials calculated by this model agree very well. The solution in stable growing pits and crevices, and propagating cracks was experimentally determined to be considerably more acidic compared to the pH of the bulk electrolyte. This evidence also supports the local acidification model.

The limitations of the model are as follows: (i) It cannot explain the specific aggressive anions ($Cl^-$, $Br^-$, and $I^-$); (ii) Localized corrosion of steels was not observed in a chloride free acidic solution (ex: sulfuric acid) although enrichment of $H^+$ in the fissures would be expected. In contrast, the specimens suffered severe localized attack in hydrochloric acid. Hence, the localized acidification model does not explain the specific action of chloride anions on pitting of steels; (iii) The increase of induction time with increasing film thickness can not be explained.

2.2.4 Stochastic pitting models

The statistical and probabilistic approaches for analyzing the scattered data of pitting (for example induction time, distribution of pit sites, etc.) are roughly divided into two groups. The first approach is simply to get the representative values or degree of variation of the distribution of scattered data
for evaluating the corrosion behavior more quantitatively. The second approach, a more important one, is to manifest a basic mechanism of pitting corrosion which exhibits intrinsically a randomness or probabilistic properties.

Detailed analyses of the scattered data of induction time for the generation of pits on stainless steel\textsuperscript{100,165,166}, high Ni alloys\textsuperscript{167,168}, Al\textsuperscript{169} and Fe\textsuperscript{98} have been reported by a number of investigators. The distribution observed in those experiments did not fit a simple exponential distribution ($P(t) = \exp(-\lambda t)$, where $P(t)$ is the cumulative survival probability pit formation, $\lambda$ is the mean pit generation rate, $t$ is the time). The plots of $\log P(t)$ and $t$ were either concave up or concave downwards (different from a linear behavior expected from the exponential distribution). The stochastic models proposed to fit the experimental data can be divided into two groups.

(A) Birth stochastic model
   (i) Simple birth stochastic model
   (ii) Plural series combination of the birth stochastic model
   (iii) Plural parallel combination of the birth stochastic model

(B) Birth and death stochastic model
   (i) Parallel birth and death stochastic model
   (ii) Series birth and death stochastic model

A schematic representation of these models is given in Figure 16.
A. Birth stochastic process

A1. Simple birth process

\[ P = e^{-(\beta - \lambda)} \]

A2. Simultaneous processes in series

\[ P = \prod_i e^{-\alpha_i (1-P)} \]

A3. Simultaneous processes in parallel

\[ P = 1 - \sum_i (1 - P_i) \]

A4. Independent processes in parallel at the constant ratio

\[ P = \sum_i P_i \]

B. Birth- and death stochastic process

B1. Birth and death process

\[ \frac{dP}{dt} = -\lambda P + \mu (1 - P) \]

\[ P = \mu (\lambda + \mu) \cdot \lambda (\lambda + \mu) \exp(-\lambda + \mu (1 - L)) \]

B2. Birth process with death process

\[ \frac{dP}{dt} = -\lambda P \]

\[ \ln P = -\lambda (t - t_0) \exp(-\mu t) \]

Figure 16 Proposed stochastic models of pitting corrosion (ref. 173)
The birth and death stochastic model was originally proposed by Williams et al.\textsuperscript{170,171} It is mathematically formulated by a probability differential equation given by

\[
\frac{dp}{dt} = -\lambda p + \mu(1-P)
\]  

(8)

because a total pit generation rate is the sum of birth probability and death probability. In the equation, \(P\) is the cumulative survival probability, \(\lambda\) is the pit generation rate, \(\mu\) is the pit repassivation rate, and \(t\) is the time). On integration of the equation (8), the survival probability can be obtained as a function of time.

\[
P = \mu(1+\mu) + (\lambda/\lambda + \mu) \exp\left[-(1+\mu(t-t_0))\right]
\]  

(9)

where \(t_0\) is the incubation time, before which no pit generation is expected. By curve fitting the above equation to the experimental survival probability vs. time plots, the parameters \(\lambda\), \(\mu\), and \(t_0\) can be evaluated. Since the experimental plots of survival probability vs. time can be easily obtained as a function of applied potential, \(\lambda\), \(\mu\), and \(t_0\) can be obtained as a function of the applied potential (E). In pitting of Fe-17 Cr binary alloys\textsuperscript{172} and Fe-17 Cr-Mo (or Ti) ternary alloys\textsuperscript{172}, it is observed that

\[
\lambda = \lambda_0 \exp(bE)
\]  

(10)

or

\[
\lambda = \alpha(E - E_{\text{crit}})
\]  

(11)
These equations suggest that the pit generation rate, $\lambda$, is strongly dependent on the applied potential. On the other hand, pit repassivation rate, $\mu$, does not show any dependence on the applied potential$^{100,165,172}$. A mass transport process is suggested to limit the pit repassivation process. According to Shibata$^{173}$, the pitting potential is the potential at which the pit generation rate, $\lambda$, is equal to the pit repassivation rate, $\mu$. Shibata found that alloying elements such as Cr, Ti, and Nb decreased only the pit generation rate, but Mo decreased the pit generation rate and increased the pit repassivation rate in ferritic stainless steels$^{100,165,172}$.

The birth and death stochastic model was supported by a Monte Carlo simulation$^{173}$ which assumes independent stochastic events of pit generation and its repassivation.

Analysis of electrochemical noise produced at the beginning of the breakdown of the passive films in the time and frequency domains revealed that the underlying statistical processes are in general more complicated than a simple poisson processes. According to Bertocci$^{174}$ and Shibata$^{173}$, the electrochemical noise can be simulated by the birth and death stochastic model.

2.2.5 Metastable and stable pitting:

Pit stability in metallic materials has received a lot of attention in recent years. Frankel$^{175}$ found that 304 type stainless steel exhibited current transients in chloride solutions at potentials far below and above the pitting potential before the onset of stable pitting. The metastable pits associated with the current transients were observed by Scanning Electron Microscope$^{176}$. Frankel$^{175,177}$ suggested that growth during metastable pitting is stabilized by the ohmic drop
associated with the porous pit cover and repassivation is expected to occur if the pit cover ruptures. The in situ microelectrode measurements\textsuperscript{178} performed on Ni suggested that the ohmic drop (IR drop) in solution at the site of localized attack is the controlling factor for the development of a stable pit before the salt film formation. If the IR drop is less than a critical value, repassivation is expected to occur. However, once a salt film is precipitated on the pit surface, stable pitting was observed.

The statistics of early pit growth in austenitic stainless steel were examined by Ezuber and Newman\textsuperscript{179} by analyzing a large number of short-lived pitting transients. By determining the plots of number of pits vs. pit current density, the authors reached the following conclusions. It was suggested that pit nucleation occurs by instability (positive feedback) in the passive current, since the pit nucleation rate was found to be proportional to the passive current density and the proportion of fast growing pits decreased as the passive current density decreased with the time. It was also suggested that early stages of pit growth are ohmically controlled, since there is a linear shift of number of pits vs. current density with potential and new nucleation sites were accessed at higher potentials. The beneficial effects of the alloying elements such as N and Mo have been attributed to a selective suppression of faster growing metastable pits. The metastable pitting in stainless steels was correlated with the semiconducting behavior of passive films existing on the metal surface\textsuperscript{180}. It is suggested that the deep localized sites in the band gap region occur where the structure of the film is heavily distorted and these locations act as nucleation sites for pit nucleation. It was found that a low number of localized states situated deep in the band gap
and a discrete distribution of localized states exist in highly resistant passive films.

Metastable pitting was also observed in Al-Cu and Al-Si thin films in dilute HF solutions\(^{181}\). Metastable pits of about 1\(\mu\)m are observed at open circuit potentials after long exposure times. In contrast, pits approaching 100 \(\mu\)m formed during the anodic polarization above the open circuit potential and the average breakdown potential. According to Scully\(^{181}\), the large ohmic drops observed within the pits control the growth of only the deep 3-dimensional pits. It was suggested that the \(\theta\)-Al\(_2\)Cu phase present in Al-Cu film has two roles: (i) It raises the potential sufficiently to promote the initiation of metastable pitting and supports the cathodic reactions to sustain pit growth; (ii) The ability of the \(\theta\)-phase to provide current was found to be critical in the growth of the metastable pits.

### 2.2.6 Critical Assessment of pitting models:

Smialowska\(^{182}\) collected all of the information pertaining to various pitting models (emphasizing both nucleation and growth aspects) and described mechanistically the possible rate controlling steps involved in the complex phenomenon of pitting.

All metallic surfaces, those of pure metals and engineering alloys, are chemically and structurally inhomogeneous. The imperfections such as flaws, pores, inclusions, precipitates, grain boundaries, dislocations are always present. The adsorption of aggressive anions are more pronounced at these locations. Localized adsorption of aggressive anions on the surface of passive films is the
first step in pitting. The passage of ions through the oxide films at the defective
sites is also relatively easy. The release of metal ions and the transport of anions
to the microdepressions existing at the defective sites results in the formation of
an aggressive environment resulting from hydrolysis. The acidic solution formed
at these discrete points first locally attacks the oxide film and later, the metal
itself. The results obtained by a scratch technique that is used to evaluate pitting
potentials, indicate that pitting is more determined by the inability of the bare
metal to be repassivated, not by the breakdown of the passivity. The pitting of
divalent metals such as Zn, Cd, and Mg can be successfully explained by the
concept of local acidification. However, the majority of structural materials
undergo pitting only in the presence of halogen ions. The specific effect of
chloride ions are (i) the ability to form complexes with cations and hydroxides; (ii)
the ability to increase the hydrogen ion concentration in the pit electrolyte; (iii) the
ability to form a salt layer on the pit bottom at low pH. All of these factors prevent
oxide formation, and the most important role played by the chloride ion is (iii).
Additionally, chloride ions may also decrease film/electrolyte energy. For pitting
to proceed, the local repassivation rate at the pit bottom must be lower than the
metal dissolution rate. The anodic potential must be high enough to induce
sufficient acidification and accumulation of chloride anions that hinder
passivation. The lowest potential necessary to satisfy these conditions would
then be the pitting potential.

On the basis of the above fundamental insights, the experimental facts
observed with pitting of metals can be easily explained.
Chapter III
Experimental procedure

3.1 Materials investigated:

Materials used in this study are

(i) Al sheet, Fe sheet, Ni foil, and 304 type stainless steel sheet
(ii) bulk Fe-Cr (7 and 18 at% Cr) and bulk Ni-Cr (7 and 24 at%) alloys
(iii) sputter-deposited Al, Fe, and Ni films
(iv) sputter-deposited Al-Cr (4 and 9 at% Cr) and Al-Ta (10 and 17 at% Ta) alloy films
(v) sputter-deposited Fe-Cr (7 and 18 at% Cr), Fe-W (11 and 19 at% W), and Fe-Ta (9, 13, and 27 at% Ta) alloy films
(vi) sputter-deposited Ni-Cr (7 and 24 at% Cr), Ni-29 at% W and Ni-21 at% Ta alloy films
(vii) sputter-deposited 304 type stainless steel film

Bulk Al (99.99% pure Al sheet), bulk Fe (99.99% pure plate), and bulk Ni (99.9+% pure sheet) were supplied by Aldrich Chemical Company. The composition (in wt%) of the commercially pure 304 type stainless steel sheet was as follows: 0.06% C, 18.5% Cr, 8.3% Ni, 1.5 at% Mn, 0.38 at% Si, 0.26% Cu, 0.36% Mo, 0.09% V, 0.14% other elements.
The targets used for the preparation of Al alloy films were obtained in the following manner. Powders of Al (99.99% pure, -325 mesh) and Cr (99.95% pure, -325 mesh) or Al (99.99% pure, -325 mesh) and Ta (99.8% pure, average particle size ~ 3μ) were mixed in the desired proportions and consolidated in vacuum at 500°C and 5000 psi. The consolidated alloy cylinders were either rolled at 450°C or cut into sheets. The sheets were then cleaned with NaOH solution or a mixture of HNO₃ & HF and isopropyl alcohol in successive steps to remove the oxide scale and other contaminants. The cleaned sheets were glued with silver epoxy to a 5 inch diameter target holder. These assemblies served as Al alloy targets. The pure Al disc was directly used as the target for the preparation of the sputter-deposited Al film.

Bulk Fe-Cr (7 and 18 at% Cr) and bulk Ni-Cr (7 and 24 at% Cr) alloys were obtained by melting the required amounts of 99.99% Cr pellets and 99.99% Fe lump or 99.9+% Ni spheres in silica crucibles in an induction furnace. The cast Fe-Cr (7 and 18 at% Cr) and Ni-Cr (7 and 24 at% Cr) alloys were used as target materials.

Pure Fe and Ni foils, and conventional 304 type stainless steel sheet were also used directly as targets for the deposition of the corresponding films.

The targets for Fe-Ta (9, 13, 27 at% Ta), Fe-W (11 and 19 at%), Ni-21 at % Ta and Ni-29 at% W alloy films were prepared in a different fashion. The above alloys were sputter-deposited from a target that consisted of a layer of perforated sheet placed on top of another non-perforated sheet. The 2 sheets were pure materials of the constituent elements in the alloy. The desired composition of the alloys was obtained by changing the relative areas of the 2
superposed sheets exposed to the ion beam. This was accomplished by varying
the number and size of the holes in the top perforated sheet. An example of this
arrangement is a perforated pure Fe sheet placed over a non-perforated pure W
sheet for obtaining an Fe-W alloy. The perforated area of the Fe sheet was
predetermined in order to achieve the required concentration of W in the alloy.

The sputtered films were obtained using a DC sputtering unit. The gas
pressure in the target chamber was initially reduced to $10^{-6}$ torr range and
filled with Ar to $8 \times 10^{-5}$ torr pressure. Pure metal or alloy films were deposited
on glass (pyrex) slides at room temperature by bombarding the corresponding
target with Ar+ ions. The accelerating voltage and ion current density were
maintained at 1 KV and 1 mA/cm², respectively. The substrate holder was
rotated during the deposition to achieve the uniform thickness and composition of
the films on all the substrates. The thickness of all of the sputtered films was
determined by mechanical (stylus) methods using a surface profile measuring
unit. The deposition rates and the thicknesses of the Al film, Al-Cr and Al-Ta films
are listed in Table 2. The thicknesses and deposition rates of Fe and Fe base
alloy films, Ni and Ni base alloy films, and 304 type stainless steel films were
approximately were 200nm and 0.33 nm/sec, respectively.

3.2 Materials Characterization:

The compositions of all of the Al, Fe, and Ni alloy films and the thickness of
the air-formed oxide on the bulk Al, Al film, Al-Cr and Al-Ta alloy films,
conventional 304 type stainless sheet, and 304 type sputtered stainless steel
Table 2

Thickness and deposition rates of Al and Al alloys

<table>
<thead>
<tr>
<th>Composition</th>
<th>Thickness (nm)</th>
<th>Deposition rate (nm/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al film</td>
<td>275</td>
<td>0.65</td>
</tr>
<tr>
<td>Al - 4 at% Cr film</td>
<td>175</td>
<td>0.42</td>
</tr>
<tr>
<td>Al - 9 at% Cr film</td>
<td>120</td>
<td>0.29</td>
</tr>
<tr>
<td>Al - 10 at% Ta film</td>
<td>130</td>
<td>0.31</td>
</tr>
<tr>
<td>Al - 17 at% Ta film</td>
<td>185</td>
<td>0.21</td>
</tr>
</tbody>
</table>
film were determined by Auger Electron Spectroscopy (AES). The concentration of alloying elements such as Cr or Ta or W in the sputtered alloy films was determined from peak to peak amplitudes\(^{183,184}\) (at 529 eV for Cr, at 166 eV for Ta, at 163 eV for W, at 68 eV for Al, at 703 eV for Fe, and at 848 eV for Ni) in the Auger spectrum and the relative sensitivity factors listed for these peaks. Identical operating conditions were maintained for the analysis of all of the samples. The thickness of the air-formed oxide on bulk Al, Al film, Al-Cr, and Al-Ta alloy films was determined from the slow sputter depth profiles, i.e., plots of peak to peak amplitude of oxidized Al signal (at 51 eV) vs. sputtering time. The thickness of the air-formed oxide on the bulk Al was assumed to be 45 Å (185). The composition of the air-formed oxide species on bulk Al, Al film, Al-Cr and Al-Ta alloy films, 304 type stainless steel sheet and 304 type stainless steel film was identified by Electron Spectroscopy for Chemical Analysis (ESCA). The spectra obtained from all the samples were compared with the standard spectra of the oxide (s) of interest. A PHI model 550 ESCA/SAM system\(^{c}\) was used for both AES and ESCA studies.

The structure of the Al film, Al alloy films, Fe film, Fe alloy films, Ni film, Ni alloy films, and 304 type stainless steel film was determined by using JEOL 200CX Analytical Electron Microscope\(^{d}\) from back thinned samples. Initially 3 mm discs were cut ultrasonically from the film / substrate specimens. The substrate side of the specimen was thinned in successive steps, rough grinding, fine grinding, and dimpling. The final step of the specimen thinning procedure, i.e., ion milling was carried out with a liquid nitrogen cold stage until the sample

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\(^{c}\) Perkin-Elmer corporation, Physical Electronics division, 6509 Flying Cloud drive, Eden Prairie, MN 55344
\(^{d}\) JEOL USA inc., Dearborn Road, Peabody, MA 01961-6043
perforated. The glass side of the sample was coated with carbon to avoid any charging of the sample in the microscope. The contamination on the metal side of the sample was removed by ion-milling at low doses for a brief period of time. Electron micrographs and diffraction patterns were taken only from those regions of the specimens containing no glass material (where Si signal in the Energy Dispersive Spectrum (EDS) is absent). The interplanar spacing (d) for any phase(s) present in the sputtered films prepared in this study can be determined from the diffraction ring pattern using the equation \( R \cdot d = L \cdot \lambda \), where \( R \) is the radius of the diffraction ring, \( L \) is the camera length (82 cm), and \( \lambda \) is the electron wavelength (0.00251 nm). The average grain size of all of the alloy films are evaluated from the electron micrographs by the Zeiss Videoplan system. The average grain size was calculated from 100 - 200 grains. The grain size of the bulk materials was estimated by comparing the respective optical micrographs to standard ASTM grain size charts.

### 3.3 Anodic Polarization Behavior

In order to conduct polarization experiments on sputtered films, two copper wires were bonded to the film with silver epoxy at two different locations. A low resistance between the two copper wires (within the metallic range) indicated good electrical contact between the film and the wire through the silver epoxy. One of the copper wires was subsequently removed and the other wire was used as the working electrode terminal. Electrical connections and the edges of the film were then coated with micro-shield lacquer, leaving an area of 0.35 to 1 cm\(^2\) exposed to the electrolyte. Platinum sheet was used as the auxiliary electrode.

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e --- Energy-Dispersive Spectrometer can be attached to the electron microscope to determine the sample composition
f --- Cal Zeiss Inc., One Zeiss Drive, Thornwood, NY 10594
All the potentials are referred to a saturated calomel electrode.

Anodic polarization tests were conducted potentiodynamically (0.125 mV/sec) in deaerated 0.1 M NaCl solution at 23 C on bulk Al, Al film, Al-Cr (4 and 9 at% Cr) and Al-Ta (10 and 17 at%) alloy films. A minimum of three specimens for each alloy composition and six specimens of Al film were used in the polarization experiments. For bulk Fe, Fe film, bulk Fe-Cr(7 and 18 at% Cr), Fe-Cr (7 and 18 at% Cr) alloy films, Fe-W (11 and 19 at% W), and Fe-Ta(9,13,27 at% Ta) alloy films, the anodic polarization curves were determined at a scan rate of 0.5 mV / sec in deaerated 0.02 M H₃BO₃ + 0.005 M Na₂B₄O₇·10 H₂O + 0.02 M NaCl solution of pH 8.5. All of the Fe base alloys and Fe were cathodically polarized for 15 sec at -1.0 V prior to anodic polarization. A coating of 0.5μ thick sputtered aluminium oxide was deposited to cover the unexposed area of the Fe-19 at% W film to prevent crevice corrosion. Anodic polarization experiments (scan rate = 0.5 mV/sec) were performed on bulk Ni, bulk Ni-Cr (7 and 24 at% Cr) alloys, Ni-Cr (7 and 24 at% Cr) alloy films, Ni-29 at% W alloy film, and Ni-21 at% Ta alloy film in deaerated 0.1 M NaCl solution. A minimum of two specimens were used in polarization experiments of Fe base and Ni base materials. Potentiodynamic (0.5 mV / sec) anodic polarization tests were performed on both the conventional 304 stainless steel sheet and the sputtered 304 type stainless steel film in aerated 0.3 wt% (~ 0.06 M) NaCl solution at 23 C. Similar tests were also conducted for the sputtered 304 type stainless steel films in aerated 1.0 M NaCl solution.
Chapter IV
Results

4.1 Auger Electron Spectroscopy:

No variation in composition across the thickness of the Al base, Fe base, and Ni base alloy films was observed from AES depth profiles. The typical AES depth profiles of Al-9 at% Cr, Fe-19 at% W, and Ni-29 at% W alloy films, after the removal of air-formed oxides are shown in Figures 17, 18, and 19, respectively. The depth profiles of both conventional and sputtered 304 type stainless steel material determined under identical sputtering conditions, after the removal of surface oxides, are presented in Figures 20(a) and 20(b), respectively. The composition of the sputtered stainless steel film was found to be the same (within 2 at%) as that of the conventional 304 type stainless steel. The thickness of the air-formed oxide species on bulk Al, Al film, Al-Cr, Al-Ta alloy films, as determined from slow sputter depth profiles of the oxide species, are listed in Table 3. The thickness of these oxide species was found to decrease with the increase in concentration of the alloying elements (Cr and Ta). The sputtering time required to remove the air-formed oxide was determined to be between 8 and 9 minutes for both of the conventional and sputtered stainless steel, under the same sputtering conditions. Hence, it was assumed that the thickness of the air-born oxide species was the same for both of these materials within the experimental error of the AES apparatus.
Figure 17  AES depth profile of Al - 9 at% Cr alloy film, after the removal of air-formed oxide.
Figure 18   AES depth profile of Fe-19 at% W film, after the removal of air-formed oxide
Figure 19   AES depth profile of Ni-29 at% W film, after the removal of air-born oxide
Figure 20 AES depth profiles of (a) Conventional and (b) Sputtered 304 type stainless steel film, after the removal of air-formed oxides.
Figure 20 (continued)

![Graph showing atomic concentration of Fe, Cr, and Ni versus sputtering time.

- **Fe**: 70 at% range, fluctuating slightly.
- **Cr**: 30 at% range, relatively constant.
- **Ni**: 10 at% range, fluctuating slightly.](image-url)
Table 3

**Characteristics of Al and Al alloys**

<table>
<thead>
<tr>
<th>Alloy composition</th>
<th>Grain size of alloys</th>
<th>Air-born oxide thickness (nm)</th>
<th>Composition of air-born oxide</th>
<th>Open circuit potential, $E_{op}$, V &lt;sub&gt;SCE&lt;/sub&gt;</th>
<th>Passive current, $i_{pass}$, μA/cm&lt;sup&gt;2&lt;/sup&gt;</th>
<th>Pitting potential $E_{np}$, V &lt;sub&gt;SCE&lt;/sub&gt;</th>
<th>$E_{np(samp)} - E_{np(bulk Al)}$, Volts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Al</td>
<td>44 μm</td>
<td>4.5</td>
<td>$\text{Al}_2\text{O}_3$</td>
<td>-0.920</td>
<td>0.8 - 7</td>
<td>-0.680</td>
<td>0.000</td>
</tr>
<tr>
<td>Al film</td>
<td>40 nm</td>
<td>5</td>
<td>$\text{Al}_2\text{O}_3$</td>
<td>-1.120</td>
<td>0.6 - 1.3</td>
<td>-0.380</td>
<td>0.300</td>
</tr>
<tr>
<td>Al-4 at% Cr film</td>
<td>20 nm</td>
<td>4.9</td>
<td>$\text{Al}_2\text{O}_3$</td>
<td>-0.950</td>
<td>0.6 - 7</td>
<td>0.150</td>
<td>0.830</td>
</tr>
<tr>
<td>Al-9 at% Cr film</td>
<td>amorphous</td>
<td>3</td>
<td>$\text{Al}_2\text{O}_3$</td>
<td>-0.940</td>
<td>0.4 - 4</td>
<td>0.350</td>
<td>1.030</td>
</tr>
<tr>
<td>Al-10 at% Ta film</td>
<td>25 nm</td>
<td>2.8</td>
<td>$\text{Al}_2\text{O}_3$</td>
<td>-1.050</td>
<td>0.4 - 7</td>
<td>0.450</td>
<td>1.130</td>
</tr>
<tr>
<td>Al-17 at% Ta film</td>
<td>2.5 nm + amorphous</td>
<td>2.1</td>
<td>$\text{Al}_2\text{O}_3 + \text{Ta}_2\text{O}_5$</td>
<td>-0.750</td>
<td>2 - 4</td>
<td>0.720</td>
<td>1.400</td>
</tr>
</tbody>
</table>
4.2 Electron Spectroscopy for Chemical Analysis:

The cationic species present in the air-formed oxide on Al and Al alloy samples is also shown in Table 3. Except for the Al - 17 at% Ta film, Al$^{3+}$ is the dominant cationic species. A mixture of Al$^{3+}$ and Ta$^{5+}$ is observed on the surface of the Al - 17 at% Ta film. Peak heights and peak areas of both Al$^{3+}$ and Ta$^{5+}$ species are observed to decrease with the sputtering time. The oxidized species of both Fe and Cr were observed in the air-formed oxide of the sputtered and conventional stainless steel. The $\text{Cr}^{\text{ox}} / \text{Fe}^{\text{ox}}$ ratio (ratio of the oxidized species of Cr to that of Fe) for the conventional stainless steel was determined to be approximately twice that of the ratio for the sputtered film.

4.3 Transmission Electron Microscopy

4.3.1 Al film, Al-Cr and Al-Ta alloy films:

The diffraction patterns and the Bright (or Dark) field images of the alloy films and the Al film are shown in Figures 21 - 25. The diffraction pattern of the Al - 4 at% Cr film can be indexed to a single phase fcc structure. The diffraction pattern of the Al - 10 at% Ta film reveals that this film predominantly consists of the supersaturated fcc solid solution. These observations suggest that the entire amount of Cr in the Al - 4 at% Cr film and most of the Ta in Al - 10 at% Ta is present in the Al solid solution (The equilibrium solid solubility limit of Cr and Ta in Al at room temperature is negligible). The Al - 9 at% Cr film is amorphous and exhibits broad, diffuse diffraction rings. Even though the diffraction pattern of the Al - 17 at% Ta film is similar to that of the Al - 9 at% Cr film, the former is mostly microcrystalline. The average grain size of the sputtered films and the bulk Al are
Figure 21  (a) Diffraction pattern, the corresponding (b) bright field image, and (c) dark field image from the first two diffraction rings of Al film
Figure 21 (continued)
Figure 22  (a) Diffraction pattern, the corresponding (b) dark field image from the first two diffraction rings of Al - 4 at% Cr film
Figure 23  (a) Diffraction pattern, the corresponding (b) bright field image of Al - 9 at% Cr film
Figure 24  (a) Diffraction pattern, the corresponding (b) dark field image from the first two diffraction rings of Al - 10 at% Ta film
Figure 25  (a) Diffraction pattern, the corresponding (b) bright field image of Al - 17 at% Ta film
listed in Table 3. Cr is found to be more effective than Ta in decreasing the grain size of the alloys.

For the case of Al - 10 at% Ta film, grain boundaries appear light in the dark field image (Figure 24b) in contrast to the display in the dark field image (Figure 21c) of single phase Al film. This indicates the presence of a second phase at the grain boundaries, which scatters (diffractions) electrons in a coherent manner. Since no additional diffraction rings were observed in the diffraction pattern (Fig. 24a), it is suggested that the diffraction rings corresponding to the grain boundary phase are superimposed on those of the supersaturated solid solution. From Figures 24(a) and 21(a), it follows that the innermost diffraction ring in Al - 10 at % Ta film is broad and diffuse in comparison to the (111) diffraction ring of the Al film. From these observations, it is tentatively put forth that the (111) diffraction ring of the supersaturated solid solution is superimposed on the broad, diffuse ring which corresponds to the amorphous phase present along the grain boundaries. It is noted that the amount of the amorphous phase is small and the differences in Figures 21(a) and 24(a) are seen more clearly from their respective high contrast negatives.

4.3.2 Fe film, Fe-Cr, Fe-W, Fe-Ta alloy films:

The selective area diffraction pattern (SAD), the bright field and dark field images of Fe film, Fe-7 at% Cr, Fe-18 at% Cr, Fe- 19 at% W, and Fe- 27 at% Ta alloy films are shown in Figures 26 to 30, respectively. The diffraction patterns of Fe film (Figure 26a), Fe-19 at% W film (Figure 29a), Fe-27 at% Ta film (Figure 30a), and most of the diffraction rings of Fe-7 at% Cr film (Figure 27a), and Fe-18 at% Cr film (Figure 28a) samples can be indexed to a single
Figure 26  (a) Diffraction pattern, the corresponding (b) bright field image, dark field images from the first (c) and third (d) diffraction rings of Fe film
Figure 26 (continued)
Figure 27  (a) Diffraction pattern, the corresponding (b) bright field image, dark field images from the first (c) and third (d) diffraction rings of Fe 7 at% Cr film
Figure 28  (a) Diffraction pattern, the corresponding (b) bright field image, dark field images from the first (c) and third (d) diffraction rings of Fe 18 at% Cr film.
Figure 28 (continued)
Figure 29  (a) Diffraction pattern, the corresponding (b) bright field image, dark field images from the first (c) and third (d) diffraction rings of Fe 19 at% W film
Figure 29 (continued)
Figure 30  (a) Diffraction pattern, the corresponding (b) bright field image, dark field images from the first (c) and third (d) diffraction rings of Fe 27 at% Ta film
Figure 30 (continued)
phase bcc structure. This suggests that the entire amount of W or Ta and most of
the Cr was present in the terminal solid solution of Fe (The equilibrium solid
solubility of Ta in Fe is less than 1 at\%\textsuperscript{186}). The diffraction patterns of Fe-19 at% W (Figure 29a) and Fe-27 at% Ta (Figure 30a) alloy films indicate the presence
of a faint, diffuse diffraction ring inside the (110) diffraction ring of the bcc phase.
The diffraction patterns of Fe-7 and 18 at% Cr alloy films also show the presence
of few diffraction rings in addition to those corresponding to the bcc phase. The
presence of these extra diffraction rings indicate the presence of additional
phase(s). Equiaxed grains were observed in all of the sputtered Fe based films
except in the case of the Fe-27 at% Ta film in which most of the grains are
elongated. The grain sizes of the bulk Fe, bulk Fe-Cr alloys and the sputtered
films of same composition are given in Table 4.

4.3.3 Ni film, Ni-Cr, Ni-Ta, and Ni-W alloy films:

The selective area diffraction patterns (SAD), the bright field and dark field
images of Ni film, Ni-7 at% Cr, Ni-24 at% Cr, Ni-29 at% W, and Ni-21 at% Ta
alloy films are shown in Figures 31 - 35. The diffraction patterns of Ni-21 at% Ta
and Ni-29 at% W alloy films and most of the diffraction rings in Ni film, Ni-7 at%
Cr film and Ni-24 at% Cr film can be indexed to a single phase fcc structure. It is
concluded that the solubility Ta in Ni has been extended beyond the equilibrium
solid solubility limit (10 at\%\textsuperscript{186}). The additional, faint diffraction rings present in
Figures 31a, 32a and 33a indicate the presence of second phase in the corresponding films. From the electron micrographs, it can be easily noticed that
the the grain size of Ni film is considerably lowered with the addition of Cr, Ta,
### Table 4

**Grain sizes of Fe base and Ni base alloys**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Grain size</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Conventional (µm)</td>
<td>Sputtered film (nm)</td>
</tr>
<tr>
<td>Fe</td>
<td>100</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>Fe 7 at% Cr</td>
<td>285</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>Fe 18 at% Cr</td>
<td>120</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>Fe-27 at% Ta</td>
<td>-----</td>
<td>38</td>
<td></td>
</tr>
<tr>
<td>Fe-19 at% W</td>
<td>-----</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>25</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>Ni-7 at% Cr</td>
<td>70</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Ni-24 at% Cr</td>
<td>145</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>Ni-29 at% W</td>
<td>-----</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>Ni-21 at% Ta</td>
<td>-----</td>
<td>9</td>
<td></td>
</tr>
</tbody>
</table>
Figure 31  (a) Diffraction pattern, the corresponding (b) bright field image, dark field images from the first (c) and third (d) diffraction rings of Ni film
Figure 32  (a) Diffraction pattern, the corresponding (b) bright field image, dark field images from the first (c) and third (d) diffraction rings of Ni 7 at% Cr film
Figure 33  (a) Diffraction pattern, the corresponding (b) bright field image, dark field images from the first (c) and third (d) diffraction rings of Ni 24 at% Cr film
Figure 33 (continued)

(c)

(d)
Figure 34  (a) Diffraction pattern, the corresponding (b) bright field image, dark field images from the first (c) and third (d) diffraction rings of Ni 29 at% W film.
Figure 34 (continued)
Figure 35  (a) Diffraction pattern, the corresponding (b) bright field image, dark field images from the first (c) and third (d) diffraction rings of Ni 21 at% Ta film
Figure 35 (continued)

(c)

(d)
and W. The average grain size of all of the sputtered films and that of bulk Ni, Ni-7 at% Cr and Ni-24 at% Cr alloys is given in Table 4.

4.3.4 304 type stainless steel film:

The selective area diffraction (SAD) pattern (Figure 36(a)) of 304 type stainless steel film reveals that this film predominantly consist of a single phase BCC structure with a lattice parameter of 0.278 nm. This value agrees well with that lattice parameter determined for the stainless steel film prepared by vapor deposition method\textsuperscript{54}. The bright field and the dark field images from the first and the third diffraction rings are shown in Figures 36(b), 36(c), and 36(d), respectively. The diffraction pattern also reveals a faint, diffuse ring indicating the presence of a second phase similar to case of the Fe base and some Ni base alloys. The grain sizes of the conventional 304 type stainless steel and of the sputtered film of the same composition are also shown in Table 5.

4.4 Anodic Polarization Behavior:

4.4.1 bulk Al, Al film, Al-Cr and Al-Ta alloy films:

Anodic polarization curves determined for Al and Al alloys in the deaerated 0.1 M NaCl solution are shown in Figure 37. For each alloy composition, the polarization curve with the highest pitting potential is plotted. The deviation in the pitting potentials of the samples for the same composition is $\pm 50$ mV. There is considerable scatter ($\pm 150$ mV) in pitting potentials of sputter-deposited Al films. However, all of these values are higher than those for the bulk Al. Because of large scatter in the pitting potentials of Al films, the polarization curve with a pitting
Figure 36. (a) Diffraction pattern, the corresponding (b) bright field and dark field images from the first (c) and third (d) diffraction rings of 304 type stainless steel film
Table 5

**Characteristics of conventional and sputtered 304 type stainless steel**

<table>
<thead>
<tr>
<th></th>
<th>Conventional</th>
<th>sputtered film</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Composition</strong></td>
<td>0.06%C, 18.5% Cr,</td>
<td>same</td>
</tr>
<tr>
<td></td>
<td>8.3% Ni, 2.8% others,</td>
<td></td>
</tr>
<tr>
<td></td>
<td>remaining is Fe</td>
<td></td>
</tr>
<tr>
<td><strong>Structure</strong></td>
<td>Single phase (FCC)</td>
<td>BCC phase + grain</td>
</tr>
<tr>
<td></td>
<td></td>
<td>boundary phase</td>
</tr>
<tr>
<td><strong>Grain size</strong></td>
<td>30 µ</td>
<td>25 nm</td>
</tr>
<tr>
<td><strong>Air-born oxide</strong></td>
<td>Cr_2O_3 + Fe_2O_3</td>
<td>Cr_2O_3 + Fe_2O_3</td>
</tr>
<tr>
<td><strong>composition</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Corrosion potential</strong></td>
<td>0.04 V_SCE</td>
<td>0.111 V_SCE</td>
</tr>
<tr>
<td><strong>Breakdown potential</strong>, E_b</td>
<td>0.3 V_SCE</td>
<td>1.15 V_SCE</td>
</tr>
<tr>
<td><strong>Mode of localized</strong></td>
<td>Crevice + Pitting</td>
<td>Crevice + Pitting</td>
</tr>
<tr>
<td><strong>corrosion</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 37 Anodic polarization curves for bulk Al, Al film, and Al alloy films in deaerated 0.1 M NaCl solution.
potential close to the average value of all the Al film samples is plotted in Figure 37. The open circuit potential, passive current density, breakdown potential (Enp, pitting potential) of the samples obtained from Figure 37 and the enhancement of the pitting potential of the alloys above that of the bulk Al are listed in Table 3 (page 84). The open circuit potential of all the samples is approximately the same except for that of the Al - 17 at% Ta film. The pitting potentials of the Al - Cr and Al - Ta alloy films are approximately 0.8V - 1.4V higher than that of the bulk Al. The pitting potential is found to increase with the concentration of the alloying elements. The pitting potential of all the Al -10 at% Ta films is observed to be consistently higher than that of Al - 9 at% Cr films, even though the difference in the pitting potentials of these alloys is 100 mV.

4.4.2 bulk Fe, Fe film, Fe-Cr alloys (bulk and sputtered), Fe-W and Fe-Ta alloy films:

Anodic polarization curves of the bulk Fe, Fe film, Fe-18 at% Cr, Fe-19 at%W, Fe-and 27 at% Ta alloy films determined in deaerated 0.02 M H_3BO_3 + 0.005 M Na_2B_4O_7·10 H_2O + 0.02 M NaCl solution are presented in Figure 38. The open circuit potentials of the bulk Fe, Fe film, Fe-19 at W, and Fe-27 at% Ta films were almost the same, whereas the open circuit potential of the Fe-18 at% Cr film was significantly higher. All of the samples exhibited active/passive transition behavior except the Fe-18 at% Cr film which did not undergo active dissolution. The passive current density of all of the film samples in Figure 38 was found to be similar. The pitting potential of Fe-18 at% Ta film is read from a plot (Figure 39) of the pitting potentials of Fe-Ta(0,9,13,27 at%) alloy films vs. the concentration of Ta. The pitting potentials of the bulk Fe, Fe film, Fe-19 at% W,
Figure 38  Anodic polarization curves for sputtered Fe film and Fe alloy films in deaerated 0.02 M $\text{H}_3\text{BO}_3 + 0.005$ M $\text{Na}_2\text{B}_4\text{O}_7.10\text{H}_2\text{O} + 0.02$ M NaCl solution ($pH = 8.5$)
Figure 39 Relationship between the pitting potential and the concentration of Ta for Fe-Ta alloy films
Fe-27 at% Ta, and Fe-18 at% Cr alloy films were determined to be 0.000 V, 0.300 V, 0.900 V, and 0.900 V, respectively.

Even though the aluminum oxide coating eliminated the crevice corrosion in the Fe-19 at% W film, a few pits which did not grow with the anodic potential were observed. As a result, an increase in current was found during the potential range of -0.2 V to 0.3 V for the Fe-19 at% W film.

Figure 40 shows the anodic polarization curves of the Fe, Fe-7 at% Cr, and Fe-18 at% Cr alloys (for both bulk materials and sputtered films) determined in deaerated 0.02 M HgBO$_3$ + 0.005 M Na$_2$B$_4$O$_7$ • 10 H$_2$O + 0.02 M NaCl solution. The open circuit potentials of the bulk Fe, Fe film, bulk Fe-Cr (7 at% Cr and 18 at% Cr) alloy samples were approximately the same, whereas the open circuit potentials of the sputtered Fe-7 at% Cr and Fe-18 at% Cr alloy films were higher than those of the other samples. Even though the passive current density of the sputtered Fe film was lower than that of bulk Fe, the pitting potentials of bulk Fe and Fe film were identical. The Fe-Cr alloys (both cast samples and sputtered films) did not show any active/passive transition unlike bulk Fe and the Fe film. The increase in the pitting potential of Fe (in the bulk state as well as nanocrystalline state) with a Cr addition is shown in Figure 41. The pitting potentials of sputtered Fe-7 and 18 at% Cr alloy films are considerably higher than those of the bulk alloys of the same composition. The increase in the pitting potential is high for the alloy of high Cr concentration (18 at%). Also, the rate of increase in the pitting potential of the Fe with an addition of Cr is higher for the sputtered films compared to the bulk samples.
Figure 40  Anodic polarization curves for Fe-Cr alloys (bulk and sputtered) in deaerated 0.02 M H$_3$BO$_3$ + 0.005 M Na$_2$B$_4$O$_7$·10H$_2$O + 0.02 M NaCl solution (pH = 8.5)
Figure 41  Relationship between the pitting potential and the concentration of Cr in Fe-Cr alloys (bulk and Sputtered)
4.4.3 bulk Ni, Ni film, Ni-Cr alloys (bulk and sputtered), Ni-Ta, and Ni-W alloy films:

The anodic polarization curves of bulk Ni, Ni film, bulk Ni-7 at% and 18 at% Cr alloys and Ni-7 at% Cr alloy film determined in deaerated 0.1 M NaCl solution are presented in Figure 42. All of these samples exhibited both pitting and crevice corrosion. The corrosion potentials of these samples are similar. The passive current densities of the sputtered films are considerably lower than for the bulk materials. The pitting potentials of the bulk Ni-Cr alloys are marginally higher than that of bulk Ni, whereas, the pitting potential of the Ni film is approximately 500 mV higher than that of bulk Ni. The pitting potential of the Ni-7 at% Cr film is slightly higher than that of the Ni film.

The polarization curves determined in deaerated 0.1 M NaCl solution for Ni-24 at% Cr, Ni-29 at% W, Ni-21 at% Ta alloy films and the Ni film exhibiting crevice corrosion are shown in Figure 43. The corrosion potentials and the passive current densities of these samples are almost the same. The breakdown potentials of Ni-29 at% W, Ni-21 at% Ta, Ni-24 at% Cr samples are -0.2 V, 0.7 V, and 0.65 V, respectively.

4.4.4 304 type stainless steel (conventional and sputtered)

Typical anodic polarization curves for both the sputtered and the conventional 304 type stainless steel samples are given in Figure 44. Both crevice corrosion and pitting were observed in these samples. The pits were mostly located at the border between the exposed metal and the insulating lacquer. Since both types of localized corrosion occur simultaneously, the potential at
Figure 42  Anodic polarization curves for Ni and Ni-Cr alloys in deaerated 0.1 M NaCl solution
Anodic polarization curves for Ni alloy films in deaerated 0.1 M NaCl solution

(All samples exhibited crevice corrosion)
Figure 44  Anodic polarization curves for 304 type stainless steel (Conventional and Sputtered) samples in aerated 0.3 wt% NaCl solution.
which the current rapidly increases will be called the breakdown potential. The breakdown potential of the conventional stainless steel is 0.3 VSCE, whereas the breakdown potential of the sputtered film of the same composition is determined to be 1.15 VSCE. The breakdown potential for the stainless steel film is very reproducible with a scatter of only ± 20 mV. Surprisingly, this film exhibits the same breakdown potential even in 1 M NaCl solution. The polarization experiments in 1 M NaCl solution were repeated for six film specimens.
Chapter V
Discussion

The optical micrographs of bulk Al do not reveal the presence of any second phase. The diffraction patterns of Al film and Al-4 at% Cr alloy film reveal no additional diffraction rings other than those corresponding to the metallic phase (either pure Al or the supersaturated fcc solid solution in case of Al-4 at% Cr film). However, there is a possibility that some of the diffraction rings corresponding to the metallic phase are superimposed on those corresponding to aluminum oxide. This is because the 'd' spacings of (200) and (220) planes of Al or the fcc solid solution matches very well with the 'd' spacings of some planes in a number of allotropic forms of aluminum oxide (Table 6)\textsuperscript{187}. Therefore, it cannot be unambiguously concluded that the aluminum oxide is absent in the Al film and the Al-4 at% Cr film from their respective diffraction patterns. A similar conclusion can also be reached for the case of Al-10 at% Ta film. Since Al-9 at% Cr film and Al-17 at% Ta film exhibit broad and diffuse diffraction patterns, it is difficult to detect any diffraction patterns corresponding to aluminum oxide, if small amounts of oxide is present.

The optical micrographs obtained for bulk Fe and the conventional 304 type stainless steel sheet do not indicate the presence of any oxide inclusions. However, the optical microscopy and electron microprobe studies performed on bulk Fe-Cr (7 and 18 at%) alloys revealed the presence of oxide inclusions in these alloys. These oxide inclusions might have formed during induction
Table 6

A comparison of interplanar ("d") spacings corresponding to the metallic phase in Al and Al alloys and the "d" values listed in the literature for aluminum oxide(ref.187)

<table>
<thead>
<tr>
<th>Alloy composition</th>
<th>(hkl)</th>
<th>&quot;d&quot;</th>
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<tr>
<td></td>
<td></td>
<td></td>
<td>phase (hkl)</td>
</tr>
<tr>
<td>Al film</td>
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<td></td>
<td>Al film</td>
</tr>
<tr>
<td>Al-4 at% Cr film</td>
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<td></td>
<td>Al-4 at% Cr film</td>
</tr>
<tr>
<td>Al-9 at% Cr film</td>
<td></td>
<td></td>
<td>Al-9 at% Cr film</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Al-10 at% Ta film</td>
</tr>
<tr>
<td></td>
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<td></td>
<td>Al-10 at% Ta film</td>
</tr>
<tr>
<td>Al film</td>
<td></td>
<td></td>
<td>δ-Al₂O₃</td>
</tr>
<tr>
<td>Al film</td>
<td></td>
<td></td>
<td>γ-Al₂O₃</td>
</tr>
<tr>
<td>Al film</td>
<td></td>
<td></td>
<td>θ₁-Al₂O₃</td>
</tr>
<tr>
<td>Al film</td>
<td></td>
<td></td>
<td>η-Al₂O₃</td>
</tr>
<tr>
<td>Al film</td>
<td></td>
<td></td>
<td>γ-Al₂O₃</td>
</tr>
<tr>
<td>Al film</td>
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<td>Al₂O₃</td>
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<tr>
<td>Al film</td>
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<td></td>
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<td>Al₂O₃</td>
</tr>
</tbody>
</table>
melting, since an iron lump was used to prepare the alloys. The diffraction patterns of Fe-Cr (7 and 18 at% Cr) alloy films, Fe-19 at% W film, and Fe-27 at% Ta film reveal additional diffraction rings indicating the presence of a second phase. The 'd' spacings for the diffraction rings corresponding to this second phase are listed in Table 7. The 'd' values calculated for the extra diffraction ring in the case of Fe-19 at% W and Fe-27 at% Ta alloy films matches with the 'd' values of the (311) plane of \( \gamma \)-Fe\(_2\)O\(_3\) and Fe\(_3\)O\(_4\) phases (Table 7). The 'd' values determined for the additional diffraction rings in the case of Fe-7 at% Cr and Fe-18 at% Cr alloy films match closely with the 'd' values for the most intense diffracting planes of iron oxides \( \gamma \)-FeO\(_3\) (\( \gamma \)-Fe\(_2\)O\(_3\)), chromium oxide (Cr\(_2\)O\(_4\)), and iron chromium oxide (FeCr\(_2\)O\(_4\)) (Table 7). Since the diffraction rings of the oxide phase in Fe-Cr alloy films are more intense than those in Fe-W and Fe-Ta alloy films, it is concluded that the excess oxide present in the Fe-Cr alloy films in comparison to that in the Fe-Ta and Fe-W alloy films originated from the bulk Fe-Cr alloy targets used for sputtering. The 'd' spacing calculated for the second phase present in 304 type stainless steel film also matches with the 'd' values corresponding to the (311) plane of iron oxides \( \gamma \)-Fe\(_2\)O\(_3\) and Fe\(_3\)O\(_4\)), (311) plane of chromium oxide (Cr\(_3\)O\(_4\)), and the (131) plane of iron chromium oxide (FeCr\(_2\)O\(_4\)) (Table 7). The intensity of the diffracting plane corresponding to the oxide phase in the stainless steel film is lower than that for Fe-Cr alloy films.

The optical micrographs of bulk Ni and bulk Ni-Cr (7 and 24 at% Cr) alloys did not reveal the existence of any oxide inclusions. However, the diffraction patterns of Ni film and Ni-Cr (7 and 24 at% Cr) alloy films indicate the presence
Table 7
A comparison of interplanar ("d") spacings corresponding to the second phase present in sputtered films prepared in this investigation and the "d" spacings listed in the literature for selected oxides.

<table>
<thead>
<tr>
<th>Material Composition</th>
<th>&quot;d&quot; values for second phase, nm</th>
<th>phase</th>
<th>&quot;d&quot;, nm (hkl)</th>
<th>l/0</th>
<th>crystal system</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-7 at% Cr</td>
<td>0.254</td>
<td>γ-Fe$_2$O$_3$</td>
<td>0.252 (311)</td>
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<td>Fe$_3$O$_4$</td>
<td>0.2532 (311)</td>
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<tr>
<td></td>
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<td>Cr$_3$O$_4$</td>
<td>0.258 (131)</td>
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<td>FeCr$_2$O$_4$</td>
<td>0.2526 (311)</td>
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<td>0.214</td>
<td>γ-Fe$_2$O$_3$</td>
<td>0.208 (400)</td>
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<td>Fe$_3$O$_4$</td>
<td>0.210 (400)</td>
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<td>Cr$_3$O$_4$</td>
<td>0.216 (400)</td>
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<td>FeCr$_2$O$_4$</td>
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<td>cubic</td>
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<tr>
<td></td>
<td>0.167</td>
<td>γ-Fe$_2$O$_3$</td>
<td>0.161 511,333</td>
<td>33</td>
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<td>Cr$_3$O$_4$</td>
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<tr>
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<td>FeCr$_2$O$_4$</td>
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<td>0.127</td>
<td>γ-Fe$_2$O$_3$</td>
<td>0.127 (533)</td>
<td>11</td>
<td>cubic</td>
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<td></td>
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<td>Fe$_3$O$_4$</td>
<td>0.127 (622)</td>
<td>4</td>
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<tr>
<td></td>
<td></td>
<td>Cr$_3$O$_4$</td>
<td>0.128 (353)</td>
<td>50</td>
<td>cubic</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FeCr$_2$O$_4$</td>
<td>0.128 (533)</td>
<td>10</td>
<td>cubic</td>
</tr>
<tr>
<td>Fe-18 at% Cr</td>
<td>0.298</td>
<td>γ-Fe$_2$O$_3$</td>
<td>0.295 (220)</td>
<td>34</td>
<td>cubic</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe$_3$O$_4$</td>
<td>0.297 (220)</td>
<td>30</td>
<td>cubic</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr$_3$O$_4$</td>
<td>0.305 (220)</td>
<td>30</td>
<td>cubic</td>
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<tr>
<td></td>
<td></td>
<td>FeCr$_2$O$_4$</td>
<td>0.296 (220)</td>
<td>33</td>
<td>cubic</td>
</tr>
<tr>
<td></td>
<td>0.257</td>
<td>γ-Fe$_2$O$_3$</td>
<td>0.257</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.219</td>
<td>γ-Fe$_2$O$_3$</td>
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<tr>
<td></td>
<td>0.167</td>
<td>γ-Fe$_2$O$_3$</td>
<td>0.167</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.129</td>
<td>γ-Fe$_2$O$_3$</td>
<td>0.129</td>
<td></td>
<td></td>
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</table>
Table 7 (continued)

<table>
<thead>
<tr>
<th>Material Composition</th>
<th>&quot;d&quot; values of this study for second phase, nm</th>
<th>Data from literature (ref. 187)</th>
<th>crystal system</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-19 at% W</td>
<td>0.257</td>
<td>Fe-19 at% W</td>
<td></td>
</tr>
<tr>
<td>Fe-27 at% Ta</td>
<td>0.264</td>
<td>Fe-27 at% Ta</td>
<td></td>
</tr>
<tr>
<td>304 stainless steel</td>
<td>0.264</td>
<td>304 stainless steel</td>
<td></td>
</tr>
<tr>
<td>Ni film</td>
<td>0.244</td>
<td>NiO</td>
<td>cubic</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NiO</td>
<td>rhombohedral</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NiO</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>NiO</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>NiO</td>
<td></td>
</tr>
<tr>
<td>Ni-7 at% Cr film</td>
<td>0.244</td>
<td>Ni-7 at% Cr film</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.146</td>
<td>Ni-7 at% Cr film</td>
<td></td>
</tr>
<tr>
<td>Ni-24 at% Cr film</td>
<td>0.244</td>
<td>Ni-24 at% Cr film</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.146</td>
<td>Ni-24 at% Cr film</td>
<td></td>
</tr>
<tr>
<td>Ni-29 at% W film</td>
<td>0.244</td>
<td>Ni-29 at% W film</td>
<td></td>
</tr>
<tr>
<td>Ni-21 at% Ta film</td>
<td>0.148</td>
<td>Ni-21 at% Ta film</td>
<td></td>
</tr>
</tbody>
</table>
of extra rings corresponding to a second phase. The 'd' values calculated for the extra rings present in the case of Ni film, Ni-7 at% and 24 at% Cr alloy films agree well with the 'd' values of the most intense diffracting planes of NiO (Table 7). It is suggested that the oxide content of the Ni film and Ni-Cr alloy films is the same, since the intensity of the diffraction rings corresponding to NiO is similar. The NiO probably formed during the sputtering process since the targets used for the preparation of the Ni film and Ni-Cr alloy films was 99.9+\% pure Ni and bulk Ni-Cr alloys prepared from Ni (99.9+\%) spheres and Cr (99.99\%) pellets respectively. It is surprising to find the presence of oxides of less reactive metals such as Fe and Ni rather than the oxides of more reactive metals such as Ta and W in the Fe and Ni based sputtered alloy films prepared in this study.

An attempt was made to determine the morphology and distribution of the oxide phase from the dark field images obtained from the diffracting rings corresponding to the oxide phase present in some of the sputtered films. If the oxide phase is present as relatively large localized particles, its detection would be easy by conventional dark field imaging techniques. However, the contrast as well as the intensity of the dark field image obtained from the diffraction rings of the oxide phase is so weak that it is not possible to distinguish the oxide phase from the matrix. It is therefore suggested that the oxide content is small and the oxide particles are very fine and uniformly distributed throughout the matrix.

From the anodic polarization behavior of Al base, Fe base and Ni-Cr alloys (Figures 37,38,40,42,44), it can be seen that the pitting potential of the alloy films strongly depends on the nature and the concentration of the alloying element.
Several investigators\textsuperscript{25,39-51,77-82} have found a strong dependence of the pitting potential of non-equilibrium Al alloys on the alloying element. Natishan et al\textsuperscript{77-82} assume that the pitting potential is determined by the chloride ion adsorption properties of the passive films present on the Al alloys. These investigators found that the pitting potential of the ion-implanted Al alloys increases with a decrease in the pH\textsubscript{Zch} of the hydrated oxide of the alloying element. The pH\textsubscript{Zch} model predicts that the surface charge of aluminum oxide can be changed by introducing the oxide forming alloying elements and thereby increasing or decreasing anion adsorption and the susceptibility to pitting. According to Davis et al\textsuperscript{25,39-42}, the pitting resistance of the co-sputtered Al-Mo, Al-Cr, Al-Ta alloys is related to the protectiveness of the passive film. The oxidized species of the corresponding alloying elements impart a greater protectiveness to the passive film against aggressive anions. The presence of these species makes the passive film more resistant to chloride attack due to an electrostatic repulsion or a modification of the oxide structure. The high pitting resistance of Al-W alloys has been attributed to a synergistic interaction between W and the hydrated aluminum oxide, which results in the formation of a more stable layer at the metal-oxide interface\textsuperscript{41}. Davis et al\textsuperscript{25,39-42} assume that the rate limiting step in localized corrosion process is ionic diffusion of chloride ions in the passive film.

The above explanations do not take all of the experimental observations in pitting of metastable Al alloys into account. From the polarization curves of co-sputtered (Figure 45) and ion-implanted Al alloys (Figure 46), it can be seen that the passive current density is similar for Al and all supersaturated alloys, even
Figure 45  Polarization curves for elemental Al and several supersaturated Al alloys in aerated 0.1 M KCl (ref. 25)
Figure 46  Anodic polarization curves for (a) Al, Al implanted Al (Al-Al) and Mo (4 at%) implanted Al and (b) Zn (12 at%) implanted Al, Al, Si (4 at%) implanted Al samples (ref. 80)
though the pitting potentials of the alloys vary over a wide potential range. It is also interesting to observe the same passive current density for Al-Mo, Al-Ta, Al-Zr and Al-Cr alloys in spite of the fact that the concentration of the oxidized solute increased five fold\textsuperscript{103,104} from the corrosion potential to the pitting potential. Hence, it is logical to conclude that the passive films on the sputtered alloys are electrochemically identical to the passive film on Al. It is likely that the defect nature and endurance of the passive films on the alloys towards aggressive anions is about the same as that of the passive film on Al. As a result, the rate determining step in pitting may not be associated either with the bulk characteristics of the passive film, or with the chloride anion adsorption characteristics of the passive film. Even though Al-W alloys (both co-sputtered and ion-implanted) exhibited the highest pitting potentials, the oxidized species of W was not observed either in the interior of the passive film or at the surface of the passive film. It seems therefore that the pitting potential is determined more by the nature of the metal / passive film interface than by the composition of the passive film. Uruchurtu and Dawson\textsuperscript{188} attributed the electrochemical noise observed at the passivation and pitting potentials of Al soon after immersion in chloride solution, to the localized breakdown and repair processes at the metal / passive film interface. The occurrence of these events indicate that the chloride ions and the water molecules reach the metal / oxide interface immediately after the sample exposure to the electrolyte.

It is well established that stable pitting in neutral chloride solutions occurs only when acidic conditions are established within the micropits. It is obvious that pit growth can proceed only when the oxide film is soluble in the acidic pit
electrolyte and is scarcely soluble in the bulk solution. In order to find a
correlation between the pitting potential of the Al alloy and the solubility of the
oxidized species of the alloying element in acidic solutions, solubility data were
collected from the literature\textsuperscript{189-192}. Since the pH within the pits of Al is close to
0.3 (pH corresponds to a saturated solution of AlCl\textsubscript{3}; existence of saturated
solution of AlCl\textsubscript{3} and a salt layer at the pit bottom has been observed for Al\textsuperscript{182}).

All solubility data was collected at pH 0. The thermodynamic solubilities were
collected from references (191) and (192). The experimental solubilities of the
alloying element oxides in acidic chloride solutions (pH = 0) were collected from
references (189) and (190). The alloying element oxides considered for the
solubilities are listed in Table 8. Since no data are available for the solubility of
TiO\textsubscript{2} . n H\textsubscript{2}O in HCl solution, the solubility in H\textsubscript{2}SO\textsubscript{4} solution at pH 0 is taken into
account. As the solubility of hydrous chromium oxide was not found in the
literature, it was indirectly estimated as follows from the work performed by Seo
et al\textsuperscript{190}. The dissolution rate constant of hydrous chromium oxide was
determined to be one-hundredth that of hydrous ferric oxide. Knowing the
solubility of hydrous ferric oxide from ref.189, the solubility of hydrous chromium
oxide was assumed to be one hundred times lower than that of ferric hydroxide.

The dependence of the pitting potential on the experimental and
thermodynamic solubilities of alloying element oxides in acidic solutions is
presented in Figures 47 and 48. Figure 47 shows the relationship between the
pitting potential of the Al alloy and the experimental solubility of the alloying
element oxide in aqueous HCl solution at pH 0. Figure 48 shows the relationship
between the pitting potential of the Al alloy and the thermodynamic solubility of
the alloying element oxide at pH 0. Both these figures indicate that the pitting
Table 8
List of alloying element oxides for which the experimental solubilities are found (ref. 189)

<table>
<thead>
<tr>
<th>Alloying Element</th>
<th>Oxide of the Alloying Element</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr</td>
<td>ZrO$_2$ . n H$_2$O</td>
</tr>
<tr>
<td>Fe</td>
<td>Fe$_2$O$_3$ . n H$_2$O</td>
</tr>
<tr>
<td>V</td>
<td>V$_2$O$_5$</td>
</tr>
<tr>
<td>Ti</td>
<td>TiO$_2$ . n H$_2$O</td>
</tr>
<tr>
<td>Mo</td>
<td>MoO$_3$</td>
</tr>
<tr>
<td>Nb</td>
<td>Nb$_2$O$_5$</td>
</tr>
<tr>
<td>Cr</td>
<td>Cr$_2$O$_3$ . n H$_2$O</td>
</tr>
<tr>
<td>Ta</td>
<td>Ta$_2$O$_5$</td>
</tr>
<tr>
<td>W</td>
<td>WO$_3$</td>
</tr>
</tbody>
</table>
Figure 47  Relationship between the pitting potential of the Al alloy 
and the experimental solubility of alloying element oxide 
in HCl solution at pH 0

(p-- Pitting potentials determined in this study) 
The other pitting potentials are collected from ref. 21,40, 42 
Alloying element concentration is approximately 4 at% except for 
Al-Ta alloy, where Ta conc. is 8-10 at%
Figure 48  Relationship between the pitting potential of the Al alloy and the thermodynamic solubility of alloying element oxide at pH 0

(p-- Pitting potential determined in this study)
The other pitting potentials are collected from ref. 40,42
Alloying element concentration is approximately 4 at%
potential increases as the solubility of the alloying element oxide in acidic solutions decreases. The increase in the pitting potential is the highest for the alloys containing alloying elements whose oxides exhibit the lowest solubilities.

Taking into account the experimental observations and the dependence of the pitting potential on solubility of alloying element oxides, the following model is proposed to explain the pitting mechanism of Al alloys. It is believed that at least a monolayer of the passive film maintains an epitaxial relationship with the metal and the defective sites in the passive film are primarily located over the grain boundaries of the underlying metal. The passive film may also contain other defects such as pores, cracks and flaws existing over the underlying dislocations or other defects on the metal surface. Electrochemical noise measurements performed by Uruchurtu and Dawson\textsuperscript{188} suggest that both chloride ions and water can migrate through the defective sites of the passive films of Al with relative ease and reach the metal surface.

Occluded cells are formed as a result of localized dissolution of the metal. The pH within the occluded cell decreases as a result of hydrolysis of Al\textsuperscript{3+} ions. Stable pits are formed when the pH goes below a critical value. This critical value of pH depends on the composition of the alloys. The effectiveness of the alloying elements in increasing the pitting potential of Al is related to the stability and solubility of the oxidized species of the alloying element in the acidic solution present in the occluded cell. For example, at pH $\sim 0$ the solubility of molybdenum oxide, chromium hydroxide, hydrated zirconium oxide, and vanadium oxide is lower than that of aluminum hydroxide. Hence, alloying elements such as Mo, Cr, Zr and V increase the pitting potential of Al by forming a
protective film in the occluded cell through oxidation. As the anodic potential is increased, the Al dissolution rate increases and the local cell pH continuously decreases by hydrolysis. Under these conditions, due to the increased solubility of the oxidation products of these alloying elements, the alloy undergoes pitting. The oxides of Ta and W are more stable than Mo, Cr, Zr, and V at zero pH, and therefore the increase in the the pitting potential of Al due to W and Ta addition is higher compared to the additions of Mo, Cr, Zr, and V.

In order to check whether the pitting model proposed for Al alloys is applicable for Fe base alloys, the pitting potentials of Fe-Cr, Fe-W, and Fe-Ta alloys containing approximately the same concentration of alloying elements are plotted against the solubility of the corresponding alloying element oxide in acidic chloride solutions (Figure 49). The oxidized species of W, Ta, Cr, and Fe considered for the solubility in acidic solutions are $WO_3$, $Ta_2O_5$, $Cr(OH)_3\cdot nH_2O$, and $Fe_2O_3\cdot nH_2O$, respectively. The solubilities of these species were collected from references (189) and (190). There are no solubility data available at pH 2 (pH observed within the pits of iron), but the experimental data are available in the quoted papers (189) and (190) at lower (for Ta, W, Cr) and higher (for Ta) pH values. Therefore the extrapolated values of solubilities at pH 2 are given in Figure 49. The pitting potentials of Fe alloy films were plotted against the solubility of alloying element oxides, as shown in Figure 49. The correlation seems to be very good and the pitting potential of the Fe alloys increases with a decrease in the solubility of the alloying element oxide similar to the case of Al alloys. To check the validity of the model (Figure 14, page 49) based on surface charge considerations and the pH of zero charge ($pH_{zch}$) of the alloying element oxide, the pitting potentials of Fe alloy films were plotted as a function of
Figure 49  Relationship between the pitting potential of the sputtered Fe alloy and the experimental solubility of the alloying element oxide in acidic solutions at pH 2
pH_{zch} of the alloying element oxide, as shown in Figure 50. According to the papers(77-82), the pitting potential should increase continuously with a decrease in the pH_{zch} of the alloying element oxide and the W should give the largest improvement in the pitting potential of Fe compared to other alloying elements. However, the highest pitting potential was obtained for the Fe-Cr and Fe-Ta films, not for the Fe-W film. Therefore, the pH_{zch} model as suggested by McCafferty and Natishan\textsuperscript{77-82} for the case for Al alloys is not applicable to Fe-base alloys. The findings of this study suggest that the pitting model proposed earlier based on the solubility of alloying element oxides for Al alloys is also applicable to Fe base alloys.

Bulk Al, all of the Al-Cr and Al-Ta films, bulk Fe, bulk and sputtered Fe-Cr (7 and 18 at% Cr) alloys, sputtered Fe-19 at% W and Fe-27 at% Ta films underwent only pitting. Both crevice and pitting were observed for bulk Ni, bulk Ni-Cr (7 and 24 at% Cr) alloys, sputtered Ni-7 at% Cr film and conventional 304 type stainless steel sheet samples. Only crevice corrosion was observed for the sputtered 304 type stainless steel film, Ni-24 at% Cr, Ni-29 at% W and Ni-21 at% Ta alloy films. The breakdown potentials of Ni-24 at% Cr, Ni-29 at% W, and Ni-21 at% Ta alloy films and the 304 type stainless steel film correspond to the oxygen evolution potentials. Since the passive current density is low over a wide potential range, crevices are formed at the oxygen evolution potentials. It is therefore concluded that Ni-24 at% Cr, Ni-21 at% Ta and 304 stainless steel films do not exhibit any pitting.

As stated in the previous paragraph, crevice corrosion is always observed for Ni-24 at% Cr, Ni-21 at% Ta, and Ni-29 at% W alloy films. Several efforts to
Figure 50  Relationship between the pitting potential of the sputtered Fe alloy and the pH of zero charge ($pH_{zch}$) of the alloying element oxide.
eliminate crevice corrosion and obtain only pitting were not successful. Since the mechanisms of the growth of crevices and the pits are similar, an attempt is made to correlate the crevice potential of these alloys with the solubility of the corresponding alloying element oxides in acidic solutions. Since the solubility of Ta and Cr oxides is low at pH 2 (it is assumed that the pH in the crevice of pure Ni is 2) compared to that of tungsten oxide, higher crevice potentials (0.7 for Ta and 0.65 V for Cr) were observed for Ni-24 at% Cr and Ni-21 at% Ta alloy films. The crevice potential of Ni-29 at% W alloy film is only -0.2 V.

It is surprising to find from Figure 42 (page 127) that the pitting potential of the Ni film is approximately 500 mV higher than that of bulk Ni. Also, the pitting potential of Ni-7 at% Cr film is considerably higher than that of bulk Ni-7 at% Cr and Ni-24 at% Cr alloys. Similarly, the pitting potentials of sputtered Fe-7 at% Cr and Fe-18 at% Cr alloy films are significantly higher than those corresponding to the bulk alloys of same composition. A comparison of the pitting and structural characteristics of few selected materials (both in the sputtered state and conventional state) is presented in Table 9. From these results, the following tentative conclusions are made. Most of the sputtered films reveal the presence of the oxide phase. The oxide is formed during the sputtering since the sputtering chamber was evacuated to a pressure of only $6 \times 10^{-6}$ torr. The fact that Fe has the same pitting potential in the sputtered (nanocrystalline) and conventional state and the Fe film does not have any oxide particles, it is clear that the pitting potential is independent of the grain size. Therefore, it seems that the oxide particles present in Fe base and Ni base alloy films listed in Table 8 might be responsible for the high pitting resistance. A fine uniform distribution of oxide
Table 9
Structural and pitting characteristics of certain selected materials prepared in the present investigation

<table>
<thead>
<tr>
<th>Composition</th>
<th>Grain size</th>
<th>Oxide species</th>
<th>Pitting potential, V&lt;sub&gt;SCF&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bulk (µm)</td>
<td>Film (nm)</td>
<td>Bulk</td>
</tr>
<tr>
<td>Al</td>
<td>44</td>
<td>40</td>
<td>-----</td>
</tr>
<tr>
<td>Fe</td>
<td>100</td>
<td>24</td>
<td>-----</td>
</tr>
<tr>
<td>Ni</td>
<td>25</td>
<td>22</td>
<td>-----</td>
</tr>
<tr>
<td>Fe 7at%Cr</td>
<td>285</td>
<td>16</td>
<td>18 µ inclusions 65% O 15-20% Cr 15-20% Si (at%)</td>
</tr>
<tr>
<td>Fe 24at%Cr</td>
<td>120</td>
<td>20</td>
<td>8 µ inclusions 65% O 15-20% Cr 15-20% Si (at%)</td>
</tr>
<tr>
<td>Ni 7at% Cr</td>
<td>200</td>
<td>3</td>
<td>-----</td>
</tr>
<tr>
<td>Ni 24at%Cr</td>
<td>90</td>
<td>7</td>
<td>-----</td>
</tr>
<tr>
<td>304 Stainless steel</td>
<td>30</td>
<td>35</td>
<td>-----</td>
</tr>
</tbody>
</table>
particles can be expected to block the metal dissolution occurring in the occluded cell and reduce the localized acidification activity. The enhanced pitting potential for the sputtered 304 stainless steel compared to the bulk material can be attributed to this effect. In order to verify this hypothesis, a high resolution electron microscopy study of unpitted and pitted sputtered alloys will be necessary. Also, sputtered films with different oxide contents can be produced by varying the partial pressure of oxygen in the sputtering chamber. If the oxide phase present in the sputtered films significantly affects the pitting potential of the metal / alloy, it is expected that there would be a variation of the pitting potential with the oxide content, and hence with the oxygen partial pressure in the sputtering chamber.
Chapter VI
Conclusions

1. (a) Both metastable Al - Cr and Al - Ta films obtained by the sputtering method exhibit excellent pitting resistance compared to bulk Al. The pitting potentials of these alloys are approximately 0.8V - 1.4V higher than that of bulk Al.

   (b) The pitting resistance of sputtered Fe-18 at % Cr and Fe-27 at% Ta alloy films is significantly higher than that of bulk Fe and Fe-19 at% W alloy film. The pitting potential of sputtered Fe-18 at % Cr and Fe-27 at% Ta alloy films is approximately 0.9 V higher than that of bulk Fe and 0.6 V higher than that of Fe-19 at% W film, respectively.

   (c) The crevice potentials of sputtered Ni-21 at% Ta and Ni-24 at% Cr alloy films are approximately 850 mV higher than that of the sputtered Ni-29 at% W film.

2. The pitting potentials of the sputtered Ni film, Ni-7 at% Cr film, Fe-7 at% Cr film, Fe-18 at% Cr film and 304 type stainless steel film are significantly higher than those of the bulk materials of the same composition. The breakdown potential of 304 stainless steel film is 1.15 V, whereas the breakdown potential of the conventional 304 type stainless steel is only 0.3 V. The higher pitting potentials of all of the above sputtered films is tentatively attributed to the
presence of very fine particles of the oxide phase that are homogeneously distributed in the alloys.

3 (a) The dependence of the pitting potential on the nature of the alloying element can be explained by the model proposed in this investigation. A very good correlation is found between the pitting potential of Al and Fe base alloys and the solubility of alloying element oxide in acid solutions with a pH corresponding to that within pits (at pH 0 for Al and at pH 2 for Fe). The pitting potential of the Al or Fe alloy is found to increase with a decrease in the solubility of alloying element oxide in acid solutions. The passive current density of Al and the Al-Cr, Al-Ta alloys was found to be similar.

(b) The crevice potential of Ni base alloy films also depends on the solubility of alloying element oxide at pH 2. The crevice potential increases with a decrease in this solubility. The passive current density of these alloys is approximately the same.
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