Chapter I

1 Introduction

Corrosion intrudes itself into many parts of our lives. A great majority of us have a personal feeling for the definition and importance of corrosion. Far too many have cringed at the emergence of rust holes in the body panels of a relatively new automobile. The outdoor rusting of steel house-hold and garden appliances is a common fact, we all have seen the stains on cooking utensils from hot foods or experienced the metallic taste in acid foods stored too long in opened cans. These effects are all caused by corrosion and are well known. This corrosion is a result of chemical reaction between a metal or metal alloy and its environment, usually a destructive one. Metal atoms in nature are present in chemical compounds (i.e. minerals). Corrosion returns the metal to its combined states in chemical compounds that are similar or even identical to the minerals from which the metals are extracted. Thus, corrosion has been called extractive metallurgy in reverse [1]. Many nonmetallic materials such as ceramics consist of metals that have their chemical reactivity satisfied by the formation of bonds with other reactive ions, such as oxides and silicates. Thus, such materials are chemically unreactive, and they degrade by physical breakdown or mechanical wear or erosion. Similarly, organic polymers (plastics) are relatively unreactive because

- **Uniform corrosion:**

A uniform regular removal of metal from the surface is the usually expected mode of corrosion. For uniform corrosion, the corrosive environment must have the same access to all parts of the metal surface, and the metal itself must be metallurgically and compositionally uniform. Uniform corrosion is preferred from a technical viewpoint because it is predictable and thus acceptable for design. Most prevalent example of uniform corrosion at a visually apparent rate is atmospheric corrosion.

- **Galvanic Corrosion**

When two dissimilar alloys are coupled in the presence of a corrosive electrolyte, one of them is preferentially corroded while the other is protected from corrosion. Any metal or alloy will be preferentially corroded when coupled to another metal or alloy with a more positive or noble potential in the Galvanic series, at the same time, the nobler alloy is protected from corrosion.

- **Crevice Corrosion**

Corrosion of a metal or alloy is often greater in the small sheltered volume of the crevice created by contact with another material. The second material may be part of a fastener (bolt, river, washer) of the same or a different alloy, a deposit of mud, sand, or other insoluble solid, or a nonmetallic gasket packing. Corrosion within in a crevice may be caused in atmospheric exposures by retention of water, while the outer surfaces can drain and dry.

- **Pitting Corrosion**

Localized attack in an otherwise resistant surface produces pitting corrosion. The pits may be deep, shallow or undercut. The stainless steels and nickel alloys with chromium depend on a passive film for corrosion resistance and are especially susceptible to pitting by local breakdown of the film at isolated sites.

- **Hydrogen damage**

Hydrogen attack is the reactions of hydrogen with carbides in steel to form methane, resulting in decarburization, voids, and surface blisters. Hydrogen blisters or smaller hydrogen cracks become evident when internal hydrogen filled voids erupt at the surface. Voids are formed when atomic hydrogen migrates from the surface to internal defects and inclusions, where molecular hydrogen gas can nucleate, generating sufficient internal pressure to deform and rupture the metal locally. Hydride formation will result in embrittlement of reactive metals such as titanium, zirconium, magnesium, tantalum, vanadium, uranium and thorium.

- **Intergranular corrosion**

In alloy reactive impurities may segregate or passivating (passivation-process by which the reaction product of the corroding element forms a barrier coating) elements such as chromium may be depleted at the grain boundaries. As a result, the grain boundary or adjacent regions are often less corrosion resistant, and preferential corrosion at the grain boundary may be severe enough to drop grains out of the surface. The best – known form of intergranular corrosion occurs in austenitic stainless steels when heat treatments deplete the grain boundaries of chromium by metallurgical reaction with carbon. The resultant structure is susceptible or "sensitized" to intergranular corrosion. In the temperature range 425°-815°C chromium carbides (mainly $Cr_{23}C_6$) precipitate at the grain boundaries, depleting the grain boundary and near by structures of chromium. Below about 10% Cr, these areas loose resistance and are corroded preferentially. Senisitization to intergranular corrosion is a common problem during welding of stainless steels.

- **Dealloying and Dezincification**

An alloying element that is active (negative electrochemically) to the major solvent element is likely to be preferentially corroded by dealloying. Selective leaching and parting are alternative terms used occasionally for the same phenomenon. The dealloying of brass, known as Dezincification, is a common and frequently cited example. Zinc is strongly active to copper and readily leaches out of brass, leaving behind relatively pure porous copper with poor mechanical properties.

- **Erosion-Corrosion**

The combination of a corrosive fluid and high flow velocity results in erosion-corrosion. The stagnant or slow-flowing fluid will cause a low or modest corrosion rate, but rapid movement of the corrosive fluid physically erodes and removes the protective corrosion product film, exposes the reactive alloy beneath, and accelerates corrosion. Sand or suspended slurries enhance erosion and accelerate erosion-corrosion attack.

1.3 Corrosion control techniques

Though there are several well-established methods available there is no single method to combat corrosion, normally more than one method is followed. The prevention steps are taken right from the design stage of the equipment or the infrastructure. Following are the general methods of corrosion prevention:

- **Materials selection**

The most common method of corrosion prevention is the selection of proper material of construction of the equipment or the infrastructure.

Following is the list of the common metals and alloys and their respective least corrosive environment in table 1.1 [2]

Table 1.1 List of most common metals and alloys and their respective environment combination.

Environment	Metal/alloy
Nitric acid	Stainless steels
Caustic	Nickel and nickel alloys
Hydrofluoric acid	Monel
Hot hydrochloric acid	Hastelloys
Dilute sulfuric acid	Lead
Nonstaining atmospheric exposure	Aluminum
Distilled water	Tin
Hot strong oxidizing solutions	Titanium
Ultimate resistance	Tantalum
Concentrated sulfuric acid	Steel

The corrosion resistance of some of the pure metals is usually better than the one containing impurity. Aluminum [3] is a good example. The commercially pure Al is used for handling hydrogen peroxide, where the presence of other elements may cause decomposition because of catalytic effects. In another case localized attack of aluminum equipment occurred because of segregation of impurity iron in the alloy. Another example is arc-melted zirconium [3], which is more corrosion resistant than induction-melted because of more impurities in the latter. This is a special case in an atomic-energy application where a little corrosion is intolerable. Non-metallic materials such as (1) rubbers, natural and synthetic; (2) plastics; (3) ceramics; (4) carbon and graphite; and (5) wood were also used to protect the infrastructure against corrosion. In general rubbers and plastics, as compared with metals and alloys, are much weaker, softer, more resistant to chloride ions and hydrochloric acid, less resistant to strong sulfuric acid and oxidizing acids such as nitric, less resistant to solvents, and have relatively low temperature limitations (80-180°C for most). Ceramics possess excellent corrosion and high temperature resistance, with the most disadvantages being brittleness and lower tensile strength. Carbons show good corrosion resistance, electric and heat conductivity, but they are fragile. Likewise wood has the limitation as being attacked by aggressive environment.

- **Altering or Changing mediums**

Altering the environment provides a versatile means for reducing corrosion. Typical changes in the medium that are often employed are (1) lowering temperature, (2) decreasing velocity, (3) removing oxygen or oxidizers, and (4) changing concentrations. In many cases these changes can significantly reduce corrosion, but they must be done with care. The effects produced by these changes vary depending on the particular system.

- **Inhibitors**

An inhibitor is a substance that, when added in small concentrations to an environment, decreases corrosion rate, an inhibitor can be considered as a retarding catalyst. There are numerous types and compositions of inhibitor. Most of them have been developed by empirical experimentation. They are proprietary and thus their composition is not disclosed. Inhibition is not completely understood because of these reasons, but it is possible to classify inhibitors according to their mechanism and composition. Following is the list of the classes of inhibitors (1) Adsorption-type inhibitors, (2) Hydrogen-evolution poisons, (3) Scavengers, (4) Oxidizers, and (5) Vapor-phase inhibitors.

Nitrogen containing organic compounds finds extensive use as an inhibitor of corrosion in various environments for example 2-mercaptobenzothiazole was found to be the most effective inhibitor to control the corrosion of nickel in nitric acid solution [4]. Corrosion of aluminum in nitric acid [5], zinc is sulfuric acid [6], copper in aqueous solution [7] are the other examples which can be sited for the use of azoles as inhibitors.

- **Design**

The design of a structure is frequently as important as the choice of materials of construction. Design should consider mechanical and strength requirements together with an allowance for corrosion. In all cases, the mechanical design of a component should be based on the material of construction. This is important, since materials of construction used for corrosion resistance vary widely in their mechanical characteristics.

- **Cathodic and Anodic protection**

Cathodic protection: Cathodic protection was employed even before the science of electrochemistry had been developed, Humphrey and Davy used cathodic protection on British naval ships in 1824[3]. Accelerated corrosion occurs if current passes from the metal to the electrolyte, thus to protect the structure the current is made to flow from the structure to the electrolyte. There are two ways of cathodic protection: (1) by an external power supply - called as impressed current method, (2) by appropriate galvanic coupling called as sacrificial anode.

Anodic Protection: This technique was developed using electrode kinetics principles. It is based on the formation of a protective film on metals by externally applied anodic currents. Metals with active-passive transitions like nickel, iron, chromium, titanium and their alloys cannot be protected by conventional cathodic protection, hence they are protected by applying carefully controlled anodic currents which results passivation of the surface.

Above listed methods are the general methods of corrosion prevention, it should be noted that materials selection, rather than the other means of preventing corrosion, play a major role in combating corrosion. Research is being continuously done in the field of protective coatings so as to increase the life of the machinery or the basic infrastructure. The advantage of protecting the substrate with a protective coating is, it reduces the amount of labor involved in finding a metal or alloy with high resistance to corrosion as well as it is economical to coat a substrate rather than building the infra structure with the material itself. Hence coating the substrate with a barrier coating or a cathodic coating finds an extensive application in industries especially the automobile industries. In this present work, two types of cathodic coatings –zinc nickel and zinc cobalt– and a barrier coating of mixed oxides of zinc and iron were synthesized and evaluated for their protective property. Following is the history and background of these methods and materials in brief.

1.4 Electrodeposition of alloys

Electrodeposition or electroplating is the process of depositing a metal from its salt solution onto another metal by passing electric current between two electrodes, one of the electrode would be the metal which is to be coated with, and this electrode is called the cathode. The second electrode is called the anode and it will be of the metal, which can be either an inert electrode like graphite, or the metal same as it is in the solution, which is called as the electrolyte. Electrodeposition is an age-old technology, which has an extensive commercial application. The commercial applications extend from decorative coatings to extraction of metals from their ores and purification of metals by slight modification of the technique according to the application, but the basic principle remains the same.

Superficially, the procedure for depositing an alloy differs in no important respect from that for depositing single metal — a current is passed from electrodes through a solution and metal deposits upon the cathode. However, the problem of finding conditions for depositing a given alloy in the form of a sound, strong, homogenous coating is not as easily solved as for a single metal. The simultaneous deposition of two or more metals without regard to the physical nature of the deposit is a relatively simple matter, for it is necessary only to electrolyze a bath of the mixed salts at a sufficiently high current density.

A preliminary and rather obvious requirement for codepositing two or more metals from aqueous solution is that at least one of the metals be individually capable of being deposited from aqueous solution. The most important practical consideration involved in the co-deposition of two metals is that their deposition potentials be fairly close together. The importance of this consideration follows from the well know fact that the more noble metal deposits preferentially, frequently to the complete exclusion of the less noble metal. To simultaneously codeposit the two metals, conditions must be such that the more negative (less noble) potential of the less noble metal can be attained without employing an excessive current density. Hence, the need for having the potentials of the two metals close together.

1.4.1 Zinc alloy plating –an overview

From a historical standpoint, the types of zinc plating processes used have changed significantly in recent years. Looking back to 1970, almost all zinc plating was done from cyanide solutions, one of the biggest changes in zinc plating over the last twenty years has been the shift from the cyanide processes to chloride processes. Due to many advantages of the chloride process (faster plating, brighter deposits, ability to plate castings), along with other problems common to earlier noncyanide alkaline systems, chloride grew to become the most prevalent type of zinc plating process. Figure 1.2 depicts clearly the shift from cyanide process to chloride process in the past twenty-year's [8]. Chloride and other non cyanide processes replaced almost 70% replacement of the cyanide process.

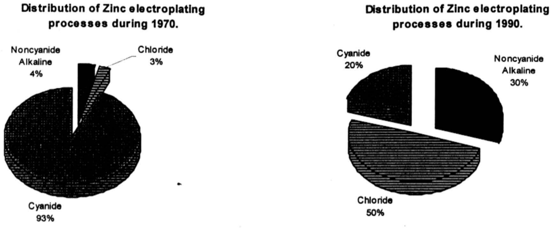

Figure 1.2 Distribution of electroplating processes.

Within chloride systems, recent advances have focused on eliminating or reducing some of the inherent limitations. New systems are available that operate with a wide range of electrolytes including sodium, potassium, and ammonium chloride, or combinations or these. Additionally some systems operate at reduced overall organic levels (1½ to 3% by volume) as opposed to earlier systems (4-5% by volume). Processes that operate at lower metal concentrations (2-3½ oz/gal; 15-26 g/l) are available offering reduced operating and waste treatment costs.

1.4.2 Anomalous codeposition of Zinc alloys

Zinc-Nickel plating is one of the best-known examples of anomalous codeposition, in which the less-noble metal deposits preferentially. The characteristics of anomalous deposition were discussed in detail by Brenner [9]. A generalized plot of the alloy composition vs. current density of anomalous codeposition consists of three regions as shown in Figure 1.3. In region I, the ratio of the less noble to the more-noble metal is smaller in the deposit than in the bath, so that deposition is not anomalous. Between regions I and II, there is an abrupt transition in deposit composition, this ratio increases sharply in the deposit from values less than P_B to values greater than P_B, which is the percentage of less noble metal in the bath. At the transition current density I_t, the bath and the deposit contain equal metal ratios. The

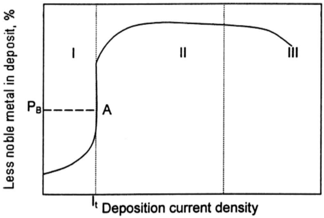

Figure 1.3 Typical plot of deposition current density versus less noble metal content in the deposit incase of an anomalous deposition

transition current is density lower when conditions favor high metal depletion in the cathode diffusion layer. In region II, the less-noble fractions are higher in the electrodeposited alloy than in the bath, i.e., anomalous deposition is observed. When region II spans a reasonably broad current density range, considerable latitude in plating rate is possible without appreciably changing the deposition composition. At still higher current densities, the less-noble metal is more depleted in the cathode diffusion layer. Diffusion does not supply the cathode with enough of the less-noble metal to maintain the region II deposit composition. Thus, in region III, increasing the deposition current density leads to a gradual drop in the fraction of less-noble metal in the deposit.

Brenner [9] summarized the most plausible hypotheses on anomalous deposition, which included the retarding influence of Zinc, deposition of the more-noble iron-group metals, the existence of a less-noble metastable state of Ni, and the role of the simultaneous hydrogen evolution. He proposed an interpretation in which an agent formed by the cathode reaction hindered deposition of the more-noble metal. Soon after Bernner' s treatise, Dahms [10] studied codeposition of the iron-group metals at the dropping mercury electrode. The high hydrogen evolution overpotential of mercury eliminated hydrogen evolution as a means of raising pH at the cathode surface. This permitted Dahms to control surface hydroxide formation by dissolving oxygen gas in the electrolyte. However, in oxygen-free electrolytes, normal codeposition occurred, the two metals depositing simultaneously without interference. Followed by this Dahms and Croll [11] investigated anomalous codeposition of nickel-iron alloys, showing that suppression of Ni^{2+} discharge began when the hydrogen evolution rate exceeded the diffusion-limited current due to H+ ions, so that metal hydroxides formed at the cathode surface. Suppression of nickel during codeposition but not during nickel alone was attributed to preferential adsorption of ferrous hydroxide, blocking the deposition of nickel but not of iron. Recently Higashi et al. [12], Imai and Kurachi [13], Horkans [14,15] have proved the same by diferent methods. It was Nicol-Philip [16] who proposed an alternative mechanism for this anomalous codeposition. Their hypothesis for deposition of one metal onto another more-noble metal is the work function difference between the two metals correlated with the difference in potential between monolayer and bulk deposition. In steady-state alloy deposition, the component metals continuously deposit on an alloy surface that is different from either of the parent metals. If the work function of the alloy is between that of the parent metals, then continuos under potential deposition of the less noble metal is possible. Although other mechanisms also have appeared to explain the anomalous codeposition of zinc, the hydroxide suppression mechanism appears to be supported by the most persuasive experimental evidence. Thus, the most likely mechanism for anomalous codeposition of zinc nickel alloy can be given as follows: at the transition current density, the pH at the cathode surface rises sufficiently to form metal hydroxides and adsorbs preferentially on the cathode. Zinc deposits readily from this adsorbed layer, but nickel deposition is retarded [17]. since it has to penetrate through the hydroxide layer.

1.4.3 Zinc/Nickel and zinc/cobalt alloys

Over the past ten years there have been numerous articles and publications that address zinc alloy plating specifically zinc nickel and zinc cobalt coatings. This increased interest is primarily because of the attention from automotive industry in its effort to provide increased service life to zinc plated components, as well as find a replacement for cadmium. Higashi [18] studied the deposition of zinc with metals of Group VIII and concluded that alloying zinc with nickel offers the best resistance to corrosion. Also the data presented by Watson [19] shows that alloys containing up to 25% nickel offers beneficial corrosion protection compared to plain zinc coating, best of the performance being offered by the alloys containing 10-13% nickel. As noted by Short et.al. [20] this alloy provides sacrificial protection to the steel. The difference in the potential protecting the steel was observed by Shibuya et.al. [21] to be approximately 100-mV a value confirmed by Wright and Gage [22] who made potentiodynamic linear polarization scans on samples immersed for six weeks in 3.5% sodium chloride solution. Several others also had worked on the zinc alloy deposition and the corrosion protection that it provides. It has been widely accepted that zinc nickel based binary alloy coating offers the best protection.

Though the fame of zinc nickel alloy still remains in peak, in recent years much of the work has been done on zinc cobalt alloy as an alternative for zinc nickel alloy coatings. Engineers are beginning to specify zinc cobalt alloy as their deposit of choice for replacement of zinc on fasteners, appliances, bicycle parts, lightning fixtures, some hand tools, furniture's, plumbing and window hardware. The reason for this choice can be listed as below [23].

- The zinc cobalt alloy plating processes are based on an acid chloride electrolyte. The process can utilize the conventional acid chloride zinc plating installations, reducing the cost of conversion substantially.
- Cobalt content in the deposit is usually 0.2 to 0.6 percent by weight as compared to conventional 10 to 12% by weight nickel in the zinc/nickel deposits. Hence it becomes less expensive to operate.
- Bright, leveled, ready acceptance of chromate conversion coatings without the usual discoloration is associated with zinc/nickel coatings.
- Absence of chelating agents in the electrolytes makes it less hazardous.
- Zinc cobalt requires only one anode source, as well as single rectifier.

- Zinc cobalt does not require the use of specially formulated chromate's, with minor adjustments in concentration, conventional chromate's can be readily used.

In view of the above listed advantages, it is apparent that zinc cobalt alloy could be a better alternative for the conventional zinc nickel plating. In this work both the choices were tried with the key interest to study the changes in the surface morphology of the coatings with variation in operating parameters.

1.4.4 Mixed oxide coating by spray pyrolysis technique

Solid films were probably first obtained in 1838 by electrolysis technique but only after 1950 it saw a burst of activity and now thin film technology has becomes an integral part of most device applications [24]. Compared to the bulk materials thin films have the advantage of nearest approximation to two dimensional structure in view of their negligibly small thickness and the large surface area to volume ratio. It is also possible to tailor the microstructure and the interface between the film and the substrate by proper selection of deposition technique and operating parameters [25]. Over the last few years development of thin film coatings on glass has been monopolized by the traditional methods of vacuum deposition such as evaporation and sputtering, which are often proved to be costly for some industrial applications [25]. The need for hard coatings spans both optical and mechanical properties. Coatings that exhibit high mechanical hardness often require simultaneously high temperature and corrosion resistance. Applications of tribological coatings include high speed cutting tools, thermal/corrosion barriers on engine parts such as combustor walls, turbine blades, exhaust linings, etc. The science of hard coating deposition is a complicated one involving not only the appropriate coating material choice, but also substrate/coating chemical, mechanical and thermal interactions. Adhesion, interface strain, internal stresses, film layer ductility, strength etc., are important parameters. Coating materials for abrasive wear/high temperature applications fall into three groups as determined by their chemical bond character: Transition Metal Oxides, Transition Metal Borides/Carbides/Nitrides and Covalent Coatings [26]. Table 1.2 lists several common materials and their properties [27,28]. Current technology permits the deposition of multilayer structures where thin layers of covalent materials are placed intermediate to the metal substrate and another hard layer(s) such as AlN, BN, etc. this way composite coatings with hardness as high as 5000 HV have been achieved [29].

Table 1.2 List of several common materials and their properties including Vickers microhardness(HV) and coefficient of thermal expansion (TCE) data.

A. Transition Metal Oxides

Coating	Hardness (HV)	TCE	Melting/Decomposition. (°C)
Al_2O_3	2100	8	2100
Al_2TiO_3	-	0.8	1900
BeO	1500	9	2550
HfO_2	780	6.5	2900
MgO	750	13	2830
Nb_2O_5	>1500	-	1400
TiO_2	1100	9	1870
Y_2O_3	~700	-	2400
ZrO_2	1200	11	2680

B. Transition Metal Borides/Carbidecs/Nitrides

Coating	Hardness (HV)	TCE	Melting/Decomposition. (°C)
LaB	2530	6	2770
LaB_6	2530	6	2770
TiB_2	3000	8	3225
W_2B_2	2700	8	2360
HfC	2700	6	3930
TaC	1500±500	6	3980
TiC	2800	8	3070
VC	2900	7	2650

B. Transition Metal Borides/Carbidecs/Nitrides			
Coating	**Hardness (HV)**	**TCE**	**Melting/Decomposition. (°C)**
WC	2200±100	4	2770
ZrC	2560	7	3440
TiN	2100	9	2950
ZrN	1600	7	2980

C. Covalent Coatings			
Coating	**Hardness (HV)**	**TCE**	**Melting/Decomposition. (°C)**
B_4C	3-4000	5	2450
BN (cubic)	4-5000	-	2730
C (diamond	7000	1	1000
SiC	2600	5	2760
Si_3N_4	1720	2.5	1900

Most of the research is being done on the nitride and carbide coatings with prime aim of improved wear resistant and protective coating [30-33].

In this present work an attempt was made to coat a mixed oxide thin film over mild steel substrate in order to study the feasibility of a possible protective coating. A novel method of coating technique, which uses only a high temperature furnace and a spraying system, was used to obtain the coating. Spray pyrolysis enables to coat metal oxide thin films or multi element metal oxide thin films with ease; which makes this technique to be the best for thin applications [34]. Since there is no need for a sophisticated equipment or high vacuum, spray pyrolysis technique is inexpensive.