

Anodic dissolution and passivation of binary alloys—An overview

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Received 18 September 2000; revised received 12 December 2001; accepted 11 January 2002

The dissolution of a metal occurs with the transfer of one or more electrons. The dissolution depends on potential, which may or may not result in passivation. In the case of dissolution of binary alloys, the dissolution may be selective for the less noble metal or simultaneous dissolution may occur. The passivation and depassivation processes on the alloy surface depend on the electrode potential and anions present in the medium. The depassivation may be uniform or with anodic breakdown at selective sites.

In 1824 Davy protected the copper sheathed ocean going ships by connecting it to zinc. Zinc dissolved sacrificially to protect the copper. In 1738 Lomonosov observed the passivation of iron in nitric acid. Schonbein in 1836 defined the "persisting alternation of corrosive characteristics" of iron as passive. The dissolution of metal or alloy is accompanied by the release of metallic ions to the solution. In presence of complexing anions in solution, solution soluble metal complexes are formed. Passivity is caused by formation of a thin, protective, hydrated oxide, corrosion-product surface film that acts as a barrier to the dissolution reaction. Depending on the potential or the oxidizing power of the solution the metal may exist in the passive or active state.

In a binary alloy an element which is active (negative electrochemically) to the major solvent element is likely to dissolve preferentially. It is reported that during World War-I dezincification of brass condensers fitted to marine engines caused more damage to the British fleet than enemy action¹. Zinc is strongly active to copper and readily leaches out of brass leaving behind relatively pure porous copper with poor mechanical properties. Copper is the most noble of the major constructional metals and selective leaching of other more active alloying elements such as nickel, silicon and aluminium are known². The other major example of dealloying is the selective leaching of iron from gray cast iron leaving behind a weak, porous network of inert graphite that can be scratched with a pen knife³.

Fe-Cr alloys form a solid solution over a wide Cr content and anodic dissolution of these alloys is found

to be uniform⁴. An alloy containing > 12% chromium exhibited the behaviour of chromium electrode in acidic medium and this was due to the specific adsorption of hydrogen or anion and also to H in alloy⁴. Fe-24Cr alloy in sulphuric acid solution exhibited passivity during anodic polarization. This was due to the preferential adsorption of passivating species at kink sites⁵.

The examination of various models on homogeneous binary alloy dissolution can be classified roughly into two groups; the one is focused on the uniform dissolution and the other on the influence of neighbour atom to the reaction kinetics. In this paper an attempt is presented to give an insight on the atomic processes taking place during dissolution and passivation.

Anodic dissolution

Studies on the kinetics of anodic or cathodic polarization usually start with the determination of the relationship between the specific process rate, expressed in terms of current densities and the shift in the potential from the equilibrium value. On anodic polarization the surface atoms are oxidized and the metal cations are liberated. The charges on the metal cations, which pass into the solution, are compensated by the charges of the anions of the electrolyte, which are transferred to the electrode surface. The salt of the given metal appears in the solution. The passivation is determined mainly by the adsorption of components of the solution mainly anions. The adsorption of OH⁻ ions or water molecules is assumed which may lead to the formation of a chemisorbed layer on the surface. If the adsorption of the oxygen of water is the reason

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for passivity, the interaction of water with the metal surface to form an adsorbed hydrated complex. Depending on the bond strength between the water and the surface atoms of the metal and the bond between these atoms and the crystal lattice, the complex may break off and pass into the solution. It is also possible that the adsorbed oxygen of the water is firmly bound to the metal surface and the anodic dissolution is inhibited. Adsorption of hydroxy ions may also follow a similar scheme.

The metal surface is comprised of the surface of individual crystallites and narrow bands of greatly disturbed crystal structure, the grain boundaries. The commercially pure metals contain metallic or non-metallic impurities either homogeneously dissolved or in heterogeneous metallic precipitate which generate defects in each individual crystallite. Dissolution takes place faster at sites where the intersection of screw dislocations takes place. Even very small amounts of impurities can cause the dissolution of high purity metals. Fig. 1 presents two-dimensional schematic diagram showing the kink sites. Dissolution takes place at kink sites. Annihilation of kinks takes place by collision of two kinds of opposite sign and generation of new kinks occur at the corner position or intersection of steps. The kink position where the particle is bound with half of the lattice energy is characterized by the fact that the growth or decomposition of the lattice always permits the appearance of another particle at the same site after each individual step. The kink site is translated during the decomposition of the lattice but remains a kink site until an atomic row in the lattice plane of the surface is completed. Fig. 2 depicts the transfer of metal ions to the electrolyte. The adatoms partially hydrated as the adsorbed layer come in contact with water molecules. The transition of a lattice atom into partially hydrated adatom and then to the fully hydrated state in the boundary layer and finally to the transport into the depth of the solution sequentially occurs.

The simplified equation for the dissolution of a pure metal is



The actual state of binding of the dissolved cation can be different. There can be $M^{z+}(H_2O)_x$ hydrated cations, which "drag along" hydrated shells consisting of xH_2O molecules. Hydrolysed cations can also be present such as $(MOH)^{(z-1)+}(H_2O)_x$ and this effect will become important for the treatment of corrosion in

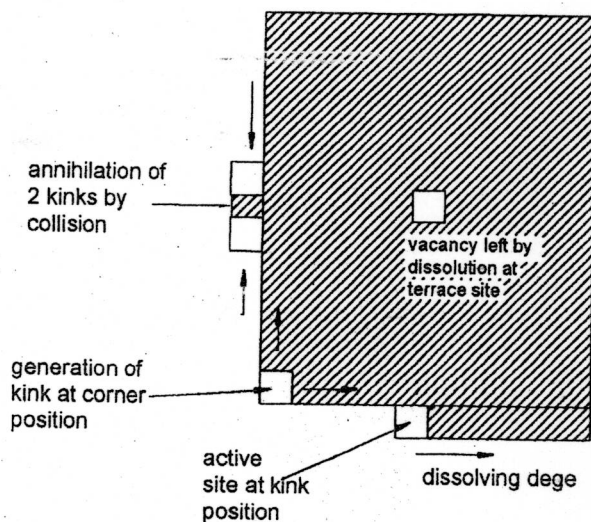


Fig. 1—Two dimensional schematic diagram showing the kink sites

crevices, cracks and holes. The bonds are formed with ligands such as ammonia and cyanides. The chemical bonding to ligands can strongly influence the kinetics of dissolution.

The first step in the dissolution process is obviously the reaction step of charge transfer, which consists of the transfer of a characteristics metal atom M_{ad} adsorbed at the metal surface to a metal cation M^{z+} in the immediate vicinity of the surface. The M_{ad} atoms are mobile in contrast to $M_{lattice}$ atoms on the lattice sites.



Eq. (2) is the proceeding reaction step for the release from the lattice; Eq. (3) is the reaction of charge transfer through the electrical double layer and Eq. (4) is the subsequent transport of the cation from the solution side of the double layer into the depth of the solution. When the sparingly soluble salt is formed the electrolyte layer near the electrode becomes saturated or even supersaturated with this salt. Super saturation leads to crystallization of the salt on the metal surface and to a gradual coating of the surface with protective salt. Such phenomenon may also lead to passivation⁶. Anodic behaviour of lead in H_2SO_4 solutions exhibits the passive film of $PbSO_4$ formed via dissolution precipitation method.

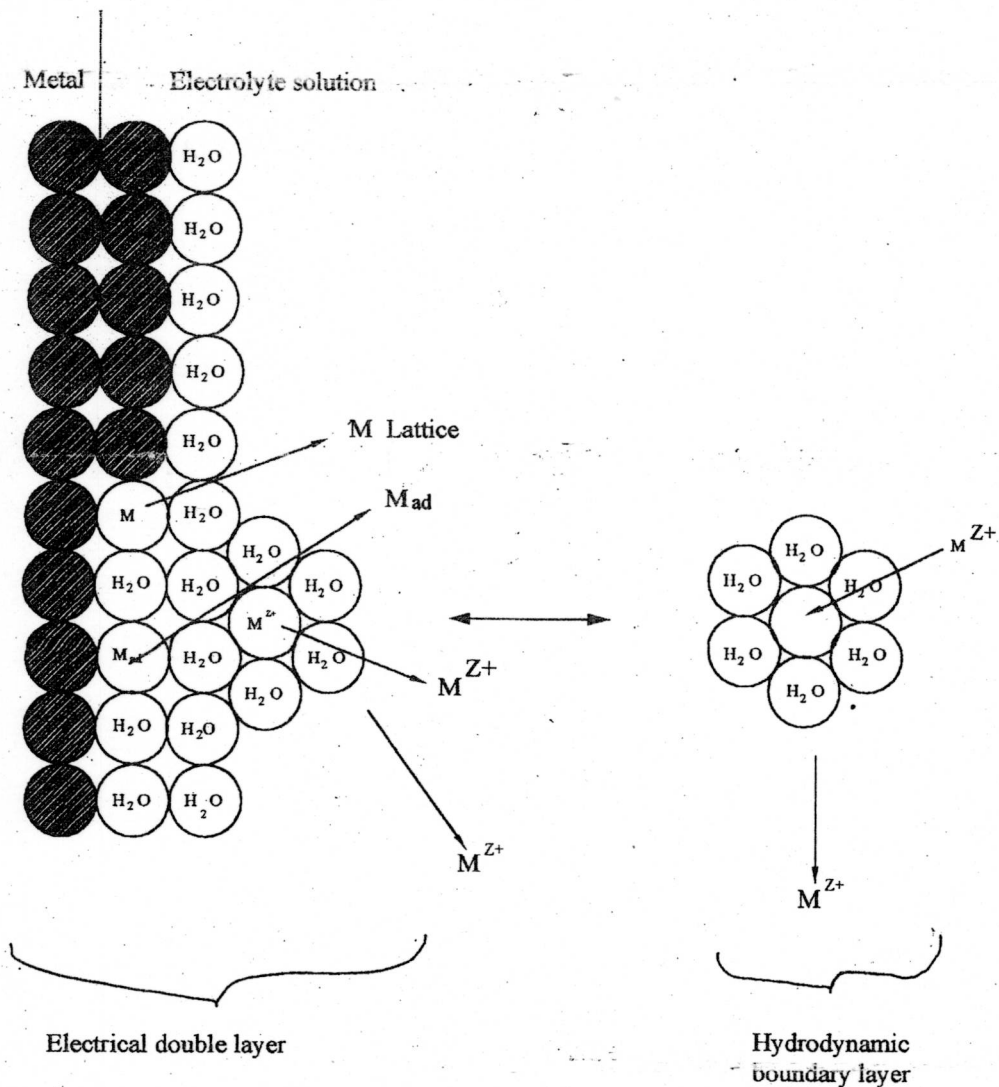


Fig. 2—Transfer of metal ions into an electrolyte solution

The anions like halides slightly affect the kinetics of anodic dissolution. At higher anodic potentials in the passive region these anions sometimes lead to depassivation and the electrode becomes non-uniformly pitted. Pure zirconium retains its passive state in pure H_2SO_4 solution. But the presence of halides dissolution takes place at higher anodic potentials causing pitting. The depassivating action of the anions decreases⁷ along the series $Cl^- > Br^- > I^-$.

Dissolution of binary alloys

The dissolution of single phase (homogeneous) binary alloys can be classified into two categories⁸.

(a) Simultaneous dissolution of the two constituent metals of the alloy

(b) Preferential dissolution of the less noble metal of the alloy with the more noble metal accumulating on the alloy surface

Simultaneous dissolution

At steady state the alloy elements go into the solution at a rate proportional to their atomic concentration in the alloy e.g. iron base stainless steels and especially ferrite Fe-Cr in which this type of dissolution occurs. The relationship between the pure components and the behaviour of these components in the alloy subject to this type of dissolution process can be given^{9,10} as algebraic sum of individual current densities.

$$I_{AB} = I_A \gamma_0 + I_0 (1 - \gamma_0)$$

... (5)

where I_{AB} is the dissolution current of an alloy AB as a function of the elementary current densities of A and B. γ_0 and $(1 - \gamma_0)$ being the atomic portion of A and B, I_A and I_B are assessed from individual curves for A and B in the same electrolyte. It was simultaneously assumed¹¹ that as a result of the alloy dissolution its surface composition, γ and $(1 - \gamma)$ could deviate from the bulk one. Consequently the proportionality of the atomic fluxes of A and B going into the solution with respect to their alloy content is expressed by

$$\frac{Z_A I_A \gamma_0}{Z_B I_B (1 - \gamma_0)} = \frac{\gamma}{(1 - \gamma)} \quad \dots (6)$$

where Z_A and Z_B are the dissolution electrovalencies. Eq. (6) yields γ_0 value matching simultaneous dissolution at any potential, I_A and I_B being known from the individual curves for A and B in the same electrolyte. Employing this method has yielded good agreement between theory and observed values¹² for several eutectic alloys and for one solid solution for Fe-Cr.

Selective dissolution

Selective dissolution of less noble components is the fundamental process of alloy dissolution. When a less noble metal dissolves it may be assumed that one or more of the three mechanisms may operate

(a) Both metals ionise followed by redeposition of the more noble metal

(b) Only the less noble metal ionises and enters the solution and atoms of the more noble metal aggregate by surface diffusion

(c) Only the less noble metal ionises and enters the solution and atoms of both metals move in the solid phase by volume diffusion.

Ionisation redeposition mechanism—The ionisation redeposition mechanism may be examined by considering the dissolution of a Cu/Zn alloy. To understand the process, Nernst equations for each reaction are discussed. In 0.1 M activity of chloride solutions and all other dissolved ions are 10^{-6} M,



$$e_{\text{Zn/Zn}^{2+}} = -0.763 + 0.0295 \log (\text{Zn}^{2+}) = -0.90 \text{ V} \quad \dots (8)$$



$$e_{\text{Cu/CuCl}_2^-} = 0.208 + 0.0591 \log (\text{CuCl}_2^-) - 0.1182 \log (\text{Cl}^-)$$

$$= -0.03 \text{ V versus SHE} \quad \dots (10)$$



$$e_{\text{CuCl}_2^-/\text{Cu}^{2+}} = 0.465 + 0.0591 \log (\text{Cu}^{2+}) / (\text{CuCl}_2^-) + 0.1182 \log (\text{Cl}^-) \quad \dots (12)$$

$$= 0.10 \text{ V for } (\text{CuCl}_2^-) \quad \dots (13)$$



$$e_{\text{Cu/Cu}^{2+}} = 0.337 + 0.0295 \log (\text{Cu}^{2+}) = 0.16 \text{ V versus SHE} \quad \dots (15)$$



$$e_{\text{CuCl/Cu}^{2+}} = 0.537 + 0.0591 \log (\text{Cu}^{2+}) + 0.0591 \log (\text{Cl}^-) = 0.12 \text{ V versus SHE} \quad \dots (17)$$



$$e_{\text{Cu/CuCl}} = 0.137 - 0.0591 \log (\text{Cl}^-) = 0.20 \text{ V versus SHE} \quad \dots (19)$$

At active potentials above -0.90 V Eq. (7) proceeds by selective dissolution of zinc from brass leaving behind a copper enriched surface. Eq. (9) is thought to initiate¹³ the dissolution of copper as potential becomes more positive (noble) than about -0.03 V which is not far removed from the experimental value of 0.0 V. As the complex ion, CuCl_2^- accumulates in solution near the surface; Cu^{2+} may be generated by Eq. (15). The half-cell electrode potential of 0.1 V is calculated assuming that (CuCl_2^-) has reached an activity of 0.01 . Oxidation to Cu^{2+} is favoured at any potential noble to the half-cell electrode potential of Eq. (11). The Cu^{2+} so formed may be reduced immediately to Cu directly by Eq. (13) or consequently with Eq. (15). If Cu^{2+} concentration increases, the half cells electrode potentials of Eqs (11), (13), (15) and (17) cannot be predicted by thermodynamics. Assuming increased (Cu^{2+}) , CuCl becomes stable when the half cell electrode potential of Eq. (13) becomes noble to that of Eq. (17) which is independent of (Cu^{2+}) and pH at $+0.2$ V for $(\text{Cl}^-) = 0.1$ M. When these potentials are maintained potentiostatically the expected deposition of metallic copper out of solution by Eq. (17) has been verified below $+0.2$ V in solutions¹⁴ containing excess Cu^{2+} . Fig. 3 presents the selective dissolution of binary alloy by ionization and redeposition mechanism.

Atomic description—If a Cu/Zn electrode is subjected to anodic dissolution there is a tendency for zinc atoms to enter the solution as ions preferentially and for copper atoms to remain at the surface in the

form of adsorbed atoms which migrate at random and may aggregate in order to form grains of nearly pure copper. Since diffusion of adsorbed copper atoms to grains of nearly pure copper requires an activity gradient, the average activity of copper on the surface may be higher than one. The steady state potential for partial equilibrium between adsorbed copper atoms and the solution may be less noble than the equilibrium potential between bulk copper and its solution. If this situation prevails, zinc and copper ions may be dissolved from a Cu/Zn electrode and copper may be plated out at the same electrode potential on the surface of copper grains, where the concentration of adsorbed copper atoms is close to the equilibrium value with the bulk crystal.

Surface diffusion mechanism—Aggregation of adsorbed atoms of the more noble metal by virtue of surface diffusion leads primarily to the formation of patches of monolayers. In addition, atoms of the more noble metal may pile up on the initial patches of monolayers and thus small three-dimensional crystals of the more noble metal may be formed. If these crystals grow in all three dimensions, there is the tendency to form finally a dense layer of the more noble metal, which prevents further anodic dissolution of the less metal. This is to be expected especially if the mole fraction of the more noble metal is high e.g. in alpha brass. Fig. 4 presents a schematic diagram of the incorporation of noble metal atom at a kink site.

Volume diffusion mechanism—This involves ionization of the less noble metal and movement of both metals in the atomic state by volume diffusion would normally be considered in operable on the basis of diffusivities extrapolated from high temperature measurements. Anodic dissolution of metal may be considered as an analogue of vapourisation of a metal¹⁵; the latter is assumed to take place in the kink-step-terrace model^{16,17} of a surface, by detachment of an atom from a kink corresponding to the formation of an adsorbed atom along the step and then along the terrace and followed by adsorption of an adsorbed atom into the gas phase. Direct vapourisation of an atom from a kink or step position is also a possible but rare event. Vapourisation of an atom from a complete lattice layer (terrace site) accompanied by formation of a surface vacancy may occur but this would require high activation energy. These events are rare. When an alloy A-B is subjected to anodic polarisation only atoms of the less noble component A enter the solution as ions. Consider a Cu-Au alloy involving

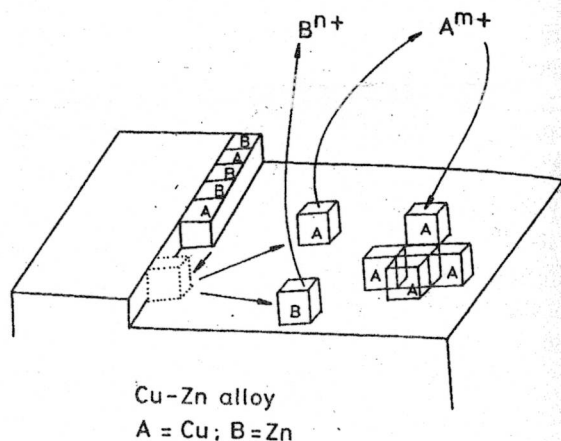


Fig. 3—Selective dissolution of a binary alloy by the ionization-redeposition mechanism

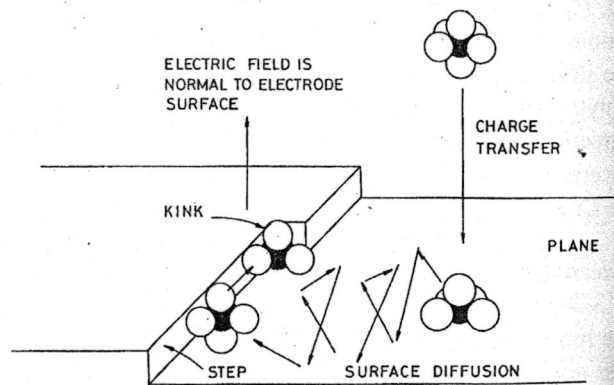


Fig. 4—Schematic diagram of the incorporation of noble metal atom at a kink site

10% Au in H_2SO_4 solution¹⁸. In this case virtually only copper enters the solution as Cu^{++} ions. A partial step on the surface with a consequence of Cu and Au atoms are shown in Fig. 5. First a copper atom from position (1) may move from its kink position in order to become an adsorbed atom and subsequently to enter the solution as an ion. Then the Au atom initially at position (2) may also move to become an adsorbed atom. Thus the Cu atom initially at position (3) becomes the last atom in the step to be ionised by the same mechanism which has been assumed for the copper atom initially at position (1) as is also true for the copper atom initially at position (4). The gold atom now at the end of the step may also move to become an adsorbed gold atom. In view of the continuous increase of the concentration of adsorbed gold atoms, there is however, an increased tendency for gold atoms to move back to the kink positions at the end of a step. Thus after removal of a sizeable fraction

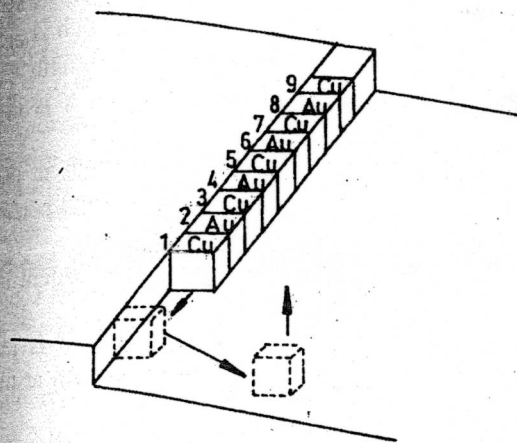


Fig. 5—Dissolution of Cu from a Cu-Au alloy via adsorbed Cu atoms as intermediate - Volume diffusion mechanism

of copper atoms from the step, it happens only very rarely that copper atom occupies the last position in a step, is free to move from its kink position and to be desorbed as an ion. Now the electrode assumes a potential considerably above the equilibrium potential. The increase in the driving force necessary to maintain a constant current may now make it possible that an atom not at the end of a step, may enter the solution as a divalent ion. As the driving force is further increased, copper atoms from complete lattice layers may enter directly into the solution as Cu^{2+} ions. In this way, surface vacancies are formed continuously. Surface vacancies in a complete lattice layer may also fill surface vacancies there by excess mono vacancies and also divacancies in the interior of the alloy may be created. The vacancies travel from the exterior of the surface and there would be vacancy gradient. The excess vacancies appearing next to the surface travel to the interior of the alloy. The volume of the crystal underneath the surface will be filled by vacancies. Diffusion of vacancies into the interior of the alloy is limited as the locations present in the interior act as sinks. In view of the continuous production of vacancies at the surface the number of available sinks for vacancies in the vicinity of the surface is reduced and subsequently excess vacancies may diffuse to greater distances from the surface while dissolution is continued.

Dissolution in the passive state—The mechanism of dissolution in the passive condition has not been ignored as many of the alloys are found to exhibit passive behaviour e.g. Cu-Ni, Fe-Cr, etc.^{19,20}. The less noble metal ions may leave the lattice and the more

noble metal continues to remain in the alloy surface or both the constituents may leave the alloy surface. The redeposition of more noble metal may take place from the solution. The redeposited layer is usually porous. The dissolution of metals may take place through this layer.

During anodic polarization, the oxidation of alloy surface takes place via solid-state oxidation or dissolution-precipitation mechanism. This oxidation causes a partial or full coverage of the surface by the passivating film mostly oxides. After completion of full coverage through the initial stages of passivation, the subsequent behaviour of passivated metals is entirely determined by the bulk properties of the passive film and the reaction at its interfaces with the metal and the electrolyte. Separation between film relaxation (growth and dissolution) and metal corrosion in the passive state is meaningless except at perfect steady state, because both aspects of metal oxidation are intimately interrelated by the charge and mass balance at the metal/film interface. The overall charge balance is expressed as

$$I = I_a + I_c \quad \dots (19)$$

where I is the external current flowing to the electrode, I_a the component of I involved in the film growth and I_c the corrosion current measuring the flux of metal cations released into the solution. At steady state, the film thickness $I_g = 0$ and external current is equal to corrosion current.

The dissolution process in the passive state involves:

- (i) Metal oxidation (ionization) at the metal/film interface.
- (ii) Transport of metal cation (and or cation vacancies) across the films.
- (iii) Metal cation transfer into solution species (solvated complexed) at the film/electrolyte interface.

Film growth can proceed at interfaces by—

- (i) Transport of oxygen anions to the metal film interface or of oxygen vacancies.
- (ii) Transport of metal cations to the film/electrolyte interface or of cations vacancies toward the metal.

Most of the models explaining film growth during dissolution have their origin in the theory of thermal oxidation initially adapted to thick oxides grown chemically or electrochemically on metals and alloys²¹⁻²³. Models differ essentially by the active par-

participation of the lattice via defects in the transport properties and consequently in the growth and dissolution reactions at interfaces. For simplicity the dissolution behaviour of passive metals can be split into two groups:

(i) Passive electrodes with a nearly constant corrosion current over an appreciable potential range. They are generally dealt with in terms of high field migration.

(ii) Passive electrodes with a potential dependent current (most commonly exhibiting a minimum) and they involve the contribution of defects.

Different models are in vogue to explain the dissolution of alloys through the passive layer and the formation of a porous dealloyed layer.

Models of passivation and depassivation—The formation of passive films and depassivation of metal or alloy surfaces was a subject of continued interest for more than one century. Extensive work has been carried out over the past hundred years to elucidate the mechanism of passivation and depassivation (the growth and breakdown) of the passive film. A vast literature exists on this subject and no attempt is made here to provide a comprehensive review. Instead only some of the more relevant models are discussed.

Passivation models

Verwey's model—Under potentiostatic conditions Verwey²⁴ studied the growth of passive films on valve metals. He observed that the decrease of electric field strength increases the film thickness and proposed a potential drop at the metal/solution interface. He assumed that the transfer of cations between adjacent lattice sites within the film was rate-controlling step.

The activation energy in the forward direction is $W - qFa\epsilon$, and that in the reverse direction is $W + qFa\epsilon$, where a is half jump distance, W is the activation energy for the slow step, q is the charge on the ion, ϵ is the electric field strength in the film and F is the Faraday constant. He deduced the total current as

$$i = i_0 [\exp qFa\epsilon/RT - \exp(-qFa\epsilon/RT)] \quad \dots (20)$$

$$= 2 i_0 \sin h [qFa\epsilon/RT] \quad \dots (21)$$

Mott and Cabrera model—As one of the earliest models^{25,26} for the growth of passive films, this model assumes:

(i) The film growth is due to the transport of metal cations across the oxide film to the film/solution interface where they react with the electrolyte.

(ii) The penetration of cations through film is assisted by the high electric field strength which is assumed to exist within the oxide [field strength $\epsilon = -d\phi/dx$; where ϕ is the electrical potential, x is the distance].

(iii) The field strength is constant throughout the film. i.e. $\epsilon = -d\phi/dx = \phi_f/L$ where ϕ_f is the total potential drop across the film of thickness L .

(iv) ϕ_f is a constant and hence is independent of film thickness.

(v) The rate limiting step for film growth is the emission of metal cations from metal into film at the metal/film interface.

The assumptions noted above yield the following expression for the differential film growth rate law,

$$dL/dt = N\Omega\gamma \exp [(-W + qa\phi_f/2L)/KT] \quad \dots (22)$$

where γ is the vibrational frequency, KT is the thermal energy, N is the number of mobile ions per unit surface area, Ω is the molecular volume per cation, W is the activation energy for the entry of cations into the film, ' q ' is the charge on the cation and ' a ' is the jump distance.

The Cabrera-Mott model has been applied extensively for interpreting the growth of oxide film on metal surfaces. However, this model tends to yield unrealistic values for the jump distance ' a ' and subsequent studies have indicated that passive films tend to grow via the movement of anions through the film to the metal-film interface, where they react with the metal.

Fehler and Mott's model—This model²⁷ invoked the following assumptions:

(i) Anion diffusion is responsible for film growth.

(ii) The rate-limiting step is the emission of an anion from the environment into the film at the film/solution interface.

(iii) The field strength in the film is independent of thickness.

(iv) The activation energy of the rate-limiting step increases linearly with thickness ($W = W^0 + \mu L$).

These assumptions yield the following differential rate law,

$$dL/dt = N\Omega\gamma \exp [(-W^0 - \mu L + qa\phi_f/2L)/kT] \quad \dots (23)$$

The principal objection to this model is that experimental evidence indicates that the interfacial reaction,



is so fast that emission of an anion from the electrolyte into the film is unlikely to be slow.

Sato and Cohen's model (Place exchange)—On the basis of their experimental work on the growth of passive films on iron in borate buffer solutions, Sato and Cohen^{28,29} proposed this model to explain the empirical rate law. The relationship between external current, i the applied potential, V_{app} and the accumulated charge in the oxide film, Q_T , is

$$i = k' \exp(mV_{\text{app}} - Q_T/n) \quad \dots (25)$$

where i is the current, V_{app} the applied voltage, Q_T is the accumulated charge and k' , m and n are parameters.

This model requires the cooperative rotation of MO pairs, thus a layer of oxygen is adsorbed onto the surface, which then exchanges places (possibly by rotation) with underlying metal atoms. A second layer of oxygen is then adsorbed and the two M-O pairs rotate simultaneously. The process is repeated and results in oxide film thickening (Fig. 6).

Depassivation models

Point defect model—Recently Chao, Lin and Macdonald have developed the point defect model (PDM) for the growth and breakdown of passive films³⁰⁻³³. The point defect model describes the growth of an anodic film and the processes that generates and annihilate vacancies at the metal/film and film/solution interfaces in terms of five electrochemical reactions (Fig. 7).

The Eqs (26), (28) and (29) are lattice conservative processes, because they do not result in any dimensional change in the film. On the other hand, Eq. (27) describes film formation but Eq. (30) results in film formation. Accordingly these processes are non-conservative.

A steady state exists only if the thickness of the film is invariant with time, which requires that the rates of the two non-conservative processes must be equal, resulting in

$$dL/dt = -(2Q/\chi)J_o|_{\text{int}} = k_o C''|_{\text{int}}|_{\text{os}} = dL/dt \quad \dots (31)$$

where χ is the oxide stoichiometry ($MO_{\chi/2}$), and J_o is the flux ($\text{mol cm}^{-2}\text{s}^{-1}$) of anion vacancies at the metal/film interface due to their generation by

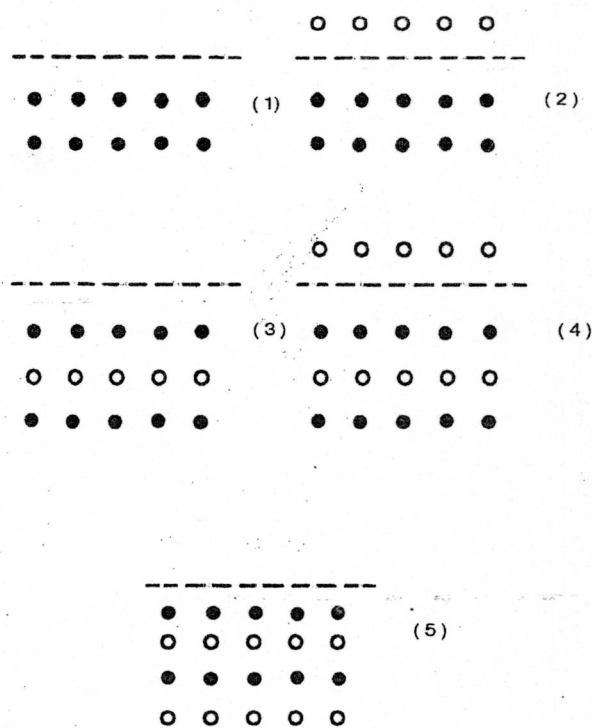


Fig. 6—Oxide film growth by the “Place exchange” mechanism • and ○ represent metal and oxygen atoms respectively. The dashed line is the solid/electrolyte interface. (1) A film free metal, (2) Oxygen adsorption on the metal surface, (3) ‘Place exchange’ between oxygen and metal, (4) Second oxygen layer is adsorbed, (5) ‘Place exchange’ between • and ○ pairs simultaneously

Eq. (27) and annihilation by Eq. (29). This model deals with the transport of cation and anion vacancies in the film. This model also predicts that the logarithmic steady state current would vary linearly with applied voltage.

The point defect model could also explain the following observations in film breakdown.

(i) A critical pitting potential exists above which localised attack is sustained, but below which pits spontaneously passivate.

(ii) In systems containing aggressive ions such as halides the breakdown potential V_c depends on the activity of the anion according to $V_c = V_c^0 - B \log a_x$, where $B > 2.303 RT/nF$.

(iii) Breakdown involves an induction time and this time decreases with pitting over potential.

(iv) The addition of aggressive ions such as Cl⁻ to a solution in contact with a passive metal causes a ‘burst’ of cations to be released from the oxide surface.

(v) The occasional transport of aggressive ions into passive films.

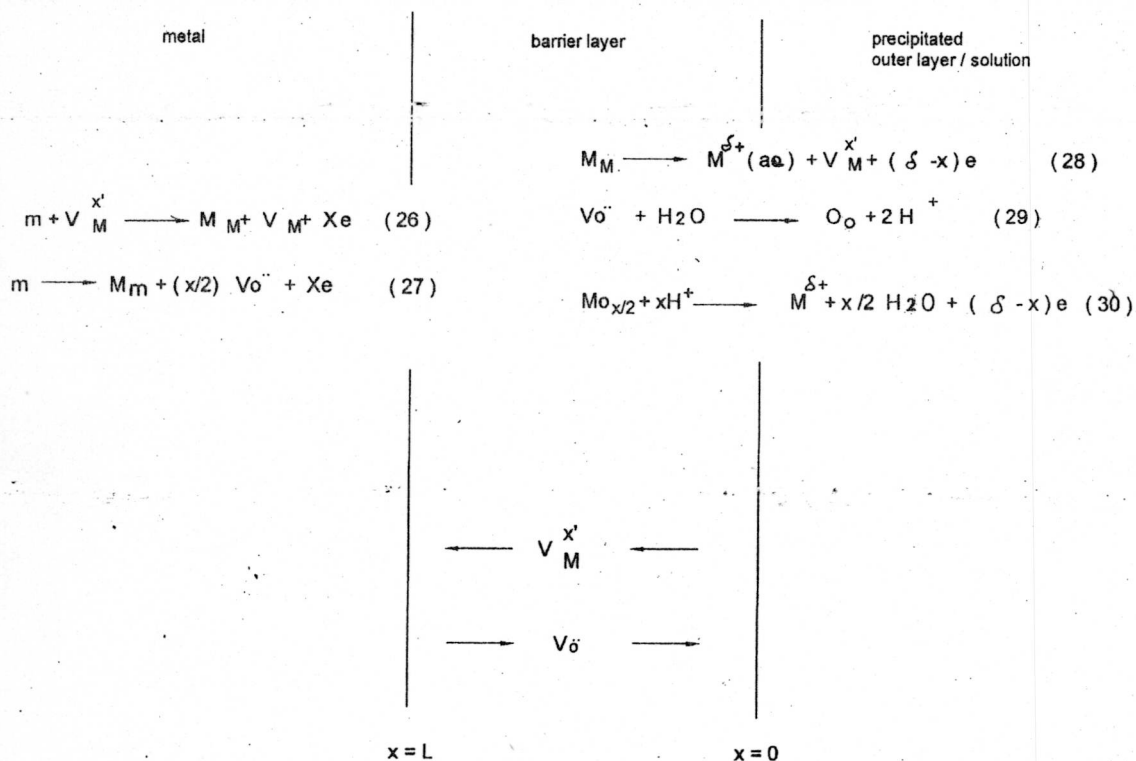


Fig. 7—Schematic representation of physicochemical process that occur within a passive film according to the PDM. m = metal atom; M_M = metal cation in cation site; O_O = oxygen ion in anion site; V_M = vacancy in metal phase; $V_M^{x'}$ = cation vacancy; V_O = anion vacancy

(vi) The size of the aggressive anions and its free energy of adsorption on to the passive film can be correlated.

Solute-vacancy-Interaction model—This is again based on point defect model. The model attempts to explain the breakdown of passive film. This model³⁴ proposes that passivity breakdown occurs because of an enhanced flux of cation vacancies from the film/solution interface to the metal/film interface. The vacancies accumulate to form a vacancy condensate at the metal /film interface which then grows to a critical size. At this time, the film collapses to form a pit that will continue to grow provided that conditions are not conducive to repassivation. The formation of the critical size of the vacancy condensate ξ that is related to breakdown potential and the induction time. Generally three processes are believed to be responsible for enhanced flux of cation vacancies.

(i) **Anion adsorption**—Anions which are comparable in size to oxide ions may adsorb into anion vacancies at the film/solution interface and the removal of anion vacancies causes a concomitant increase in the concentration of cation vacancies. This is a primary process in the case of breakdown of passive films by chloride ions.

(ii) **Electrochemical cation dissolution**—When the applied anodic potentials are high cations may be ejected from the film/solution interface. The necessary condition is that the cation formed on dissolution exists in a higher oxidation state than does in the film. This process is charge transfer controlled and cation vacancies at the film/solution interface will increase dramatically, which may be identified with the breakdown potential.

(iii) **Electro-dissolution of inclusions**—Inclusions such as sulphides in carbon steels and stainless steels may cause break down of passive films. The pit nucleation occurs via the creation of cation vacancies. For example in carbon steels the electro-dissolution of the manganese from the sulphide particles creates cation vacancies.

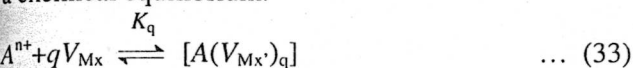
One consequence of the diffusion of metal cations from the m/f interfaces is that metal vacancies (or metal holes) are created at the metal/film interface. These metal “holes” will tend to submerge into the bulk of the metal and hence to “disappear”. However when the cation diffusion rate (i.e. metal hole production rate) is higher than the rate of “metal hole” submergence into the bulk the metal holes will start piling up and hence will form a void at the metal/film

interface. This is the process of pit incubation. When the void grows to a certain critical size, the passive film suffers local collapse, which then marks the end of pit incubation period. Subsequently the collapsed site dissolves much faster than any other place on the surface thereby leading to pit growth. Now the criterion for pit initiation can be expressed as,

$$(J_{ca} - J_m) \times (t - \tau) \geq \epsilon \quad \dots (32)$$

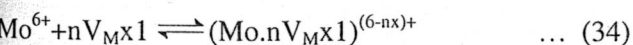
where J_{ca} is the cation diffusion rate in the film, J_m is the rate of submergence of the metal holes into the bulk metal, t is the time required for metal holes to accumulate to a critical amount, ϵ (i.e. t is the incubation time) and τ is a constant. τ is introduced to account for diffusion during the transient period and it is a measure of the time over which transient diffusion is significant compared with steady state diffusion.

The interaction between cation vacancies (V_{Mx}) and a solute ion (A^{n+}) in the passive film is represented as a chemical equilibrium.



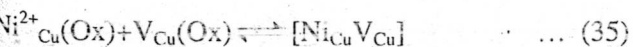
where K_q is the equilibrium constant. $K_q = (p)(A)/(v) q$ in which (p) , (A) and (v) are the concentrations of complex, solute and vacancy respectively. The condition for film breakdown remains as stated above.

The highly charged solute in the passive film, such as Mo^{6+} , can form complexes with the negatively charged cation vacancies²⁴,



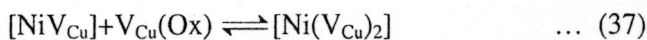
The complex formation decreases not only the concentration of free cation vacancies in the film but also the diffusivity of these species.

The model proposes pairing of highly charged solute (nickel) ions substitutionally present in the barrier layer and mobile cation vacancies. If we assume that nickel is incorporated in the form of Ni^{2+} ions, the resulting solute has a charge of +1. Charged solutes would electrostatically interact with oppositely charged mobile cation vacancies.



The reaction leads to the formation of a neutral species. There may be a possibility of nickel species of higher valency, i.e. Ni^{3+} may be present in the

layer. According to the SVIM model that would imply the formation of +2 charged solute namely



The electrostatic interaction between the solute and a mobile cation vacancy is greater for highly charged solutes and also the total number of vacancies that may be complexed. Increase in the valency of the substituent element will increase the rise in electronic resistivity per substitution. Diffusivity and concentration of the mobile cation vacancies in the layer would decrease with complexation.

The SVIM tries to explain^{34,35} partially the following observations:

(i) Breakdown of passive films in Fe/Cr/Ni alloys with electro-dissolution of chromium.

(ii) The addition of smaller alloying elements to the alloy phase to improve the pitting resistance. For example the addition of Mo and W to the Fe/Cr/Ni alloys.

(iii) The observed synergism between chromium and molybdenum content to protect Fe-Cr-Ni austenitic steels in aggressive media.

Conclusion

Binary alloy may dissolve either selectively or uniformly. The simultaneous dissolution of both components may occur and the nobler metal may deposit. The removal of both components from steps or kink sites may also accompanied with the formation of adatoms of noble component. The alloy component during dissolution creates excess cation vacancies. The formation of new phase during anodic polarization involves the transport of cations across the film and the film thickening depends on applied potential. The anion diffusion may cause the film thickening. The annihilation of cation vacancies may occur at the metal/film and film/solution interface. The anions transport facilitated by applied potential may cause film rupture. The cation vacancies accumulate at the metal/film interface leading to film breakdown by pit formation. The minor alloying elements react with cation vacancies and also cause film breakdown.

The ideas presented above take into account the solid-state approach. The roles of anion and cation vacancies, transport of aggressive and passivating anions and the electric field on the film formation are discussed. The adsorption of anions and the chemical

nature of the metal complexes formed would also decide the film breakdown. The charge on the anions would decide the complexes formed at the film/solution interface and their relative stability. The surface chemical processes also play an active role in the alloy dissolution, passivation and depassivation. A complete picture would emerge if solution chemistry were also taken into account.

Acknowledgement

One of the authors J. Mathiyarasu expresses his sincere thanks to CSIR, New Delhi for the award of fellowship (SRF).

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