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Cathodic modification as a means of improving the corrosion resistance of alloys

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Cathodic modification is defined and its origin is discussed. The criteria necessary for cathodic modification are listed for the base alloy as well as the cathodic alloying component, and the principle of cathodic modification is treated in detail. The mechanism of cathodic modification is also described extensively. Various mechanisms that account for the redistribution of alloying elements on the corroded surface are compared and discussed, and the most likely one is pointed out. It is concluded that cathodic modification is a very powerful electrochemical means of improving the corrosion resistance of alloys, particularly of stainless steels and titanium-based alloys in non-oxidizing acid media.

Nomenclature

i_p Passive current density
i_{cr} Critical current density
i_{co} Corrosion current density
i_{cath} Current density of cathodic process

i_{tr} Transpassive current density
E_{co} Corrosion potential
E_p Passivation potential
E_0^A Anodic potential of base metal or alloy
E_0^C Potential of cathodic component
E_{tr} Transpassive potential

1. Introduction

During the course of the past thirty years, a number of papers concerning the application of cathodic modification and the corrosion behaviour of cathodically modified alloys has been published, especially by the Tomashov group in the USSR. However, none of these provides a comprehensive description of the electrochemistry of the cathodic modification phenomenon and of the mechanisms involved. The purpose of this review, therefore, is to present in detail all aspects concerning the electrochemistry of cathodic modification. The practical applications of cathodic modification in different alloy systems, and the corrosion behaviour of cathodically modified alloys in different acidic media, will be dealt with in a subsequent review.

An examination of the mechanisms of corrosion processes by Tomashov [1] indicates that there are four possible ways in which corrosion–resistant alloys can be produced and the resistance of alloys against electrochemical attack increased, namely:

(a) an increase in the degree of thermodynamic stability;

(b) retardation of the kinetics of the cathodic processes;

(c) retardation of the kinetics of the anodic processes; and

(d) the production of stable passivating oxide layers.

The thermodynamic stability of commercial steels can be increased in only a limited number of cases, for example, chromium-containing steel can be alloyed with a nickel or molybdenum [1, 2]. Cathodic reactions can be retarded in two ways: by the elimination from alloys of active cathodic impurities, such as iron or copper in zinc, and by increase of the overvoltage of the cathodic process, for example, in the alloying of manganese or zinc to magnesium alloys, and of arsenic or antimony to steel. Stable passivating oxide

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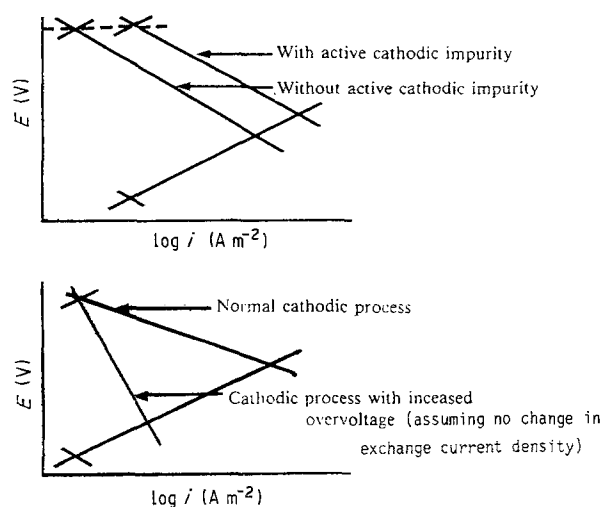
Fig. 1. Schematic representation of ways in which cathodic reactions can be retarded.

Fig. 2. Schematic illustration of the effect of cathodic modification.

layers can be obtained by adding chromium, which is thermodynamically less stable than iron, to iron to produce stainless steel which owes its corrosion resistance to the formation of passivating oxide layers on the surface of the steel. Retarded cathodic reactions can change the polarization curves as shown in Fig. 1.

The anodic reaction can be retarded as the result of an increase in the ability of the alloy to be passivated. This can be done in various ways, including the alloying of iron, nickel and ferronickel steels with chromium, or the introduction of active cathodes into the alloy, e.g. the alloying of stainless steels and titanium with platinum group metals (PGMs). The latter technique is known as cathodic modification.

2. Origin of cathodic modification

Cathodic modification is not widely known and practised outside the USSR, but it is by no means a new discovery or concept. As early as 1911, Monnartz [3] reported that the rapid corrosion of iron–chromium alloys in certain acids can be prevented either by the winding of a platinum wire around the sample used in the corrosion test, or by alloying of the steel with platinum. Nobody seems to have shown much interest in this discovery until Tomashov et al. [4] first confirmed it in 1948, and then further developed the concept of 'cathodic alloying' in their work on stainless steels and titanium and its alloys. Other contributions have been made mainly by Stern and co-workers [5–9] and Cotton [10–12].

In principle, passivity can be induced in a base metal or an alloy by the addition of a noble metal (one of the PGMs, gold, or silver) having a high cathodic exchange current density, provided that the passive region of the base alloy extends to potentials that are more negative than the redox potential of the environment. This is schematically represented in Fig. 2, where line A represents the cathodic polarization curve for the metal and B that for the cathodically modified alloy. Hence, for metals and alloys that
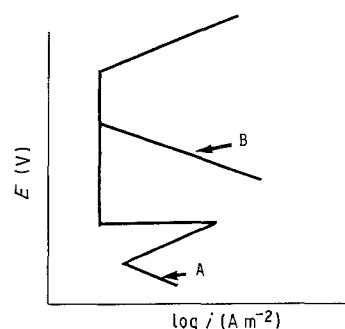
exhibit stable passivity at potentials sufficiently more negative than the existing hydrogen potential in the system, spontaneous passivation will be possible in the absence of any substance or compound more oxidizing than hydrogen ions. The effect of cathodic modification should therefore be most pronounced in non-oxidizing acid environments, for example, deaerated hydrochloric and sulphuric acids.

This conclusion has been confirmed by Greene et al. [9] who found that, while addition of PGMs to chromium in non-oxidizing acids (hydrochloric and sulphuric acids) improved its corrosion resistance, they had a detrimental effect in oxidizing acid (nitric acid) because the oxidizing acid increased the potential to a value in the transpassive range.

3. Requirements for cathodic modification

The basic conditions required for successful cathodic alloying can be summarized as follows [1]:

(1) The base alloy must have a small critical current density (i_{cr}) that will be easily exceeded by the current of the hydrogen cathodic reaction on the added noble metal at the given passivation potential (E_p).

(2) The passivation potential (E_p) of the base metal must be sufficiently negative to allow the cathodic component that has been introduced to change the corrosion potential (E_{co}) of the alloy to a value in the passive range that is more positive than E_p but less positive than the potential associated with the onset of transpassive processes (E_{tr}).

(3) The transpassive potential (E_{tr}) of the base alloy should be sufficiently electropositive to allow a wide passive range.

Furthermore, the cathodic alloying component should itself satisfy certain basic conditions [1]: it should have a higher exchange current density i_0 (and lower overvoltage) for the cathodic process of hydrogen evolution than the base metal or the alloy, and it should be corrosion resistant under the given conditions.

In non-oxidizing acids (such as sulphuric and hydrochloric acids) the condition requiring a sufficiently negative passivation potential is satisfied by stainless steels, chromium based alloys and titanium-based alloys, while the PGMs have the necessary high exchange current density, i_0 (and low overvoltage), for hydrogen evolution.
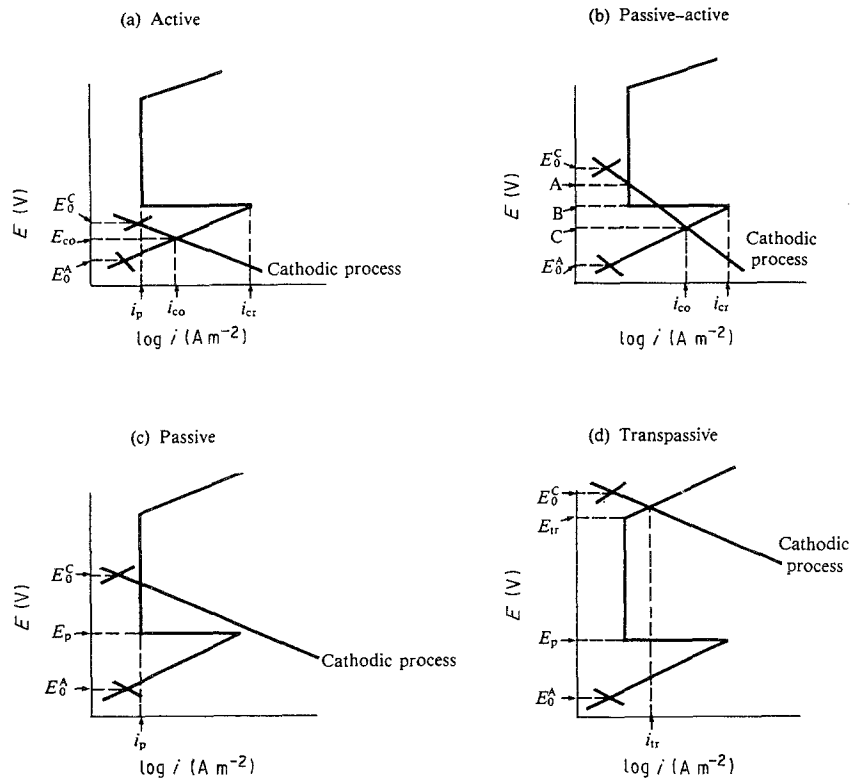
Fig. 3. Different active-passive states in an alloy system.

4. Principle of cathodic modification

Figure 3 presents schematic diagrams of the four distinct states that can be displayed by a system with an active–passive transition. The different states depend upon the relative efficiency of the cathodic process (or processes) in each case.

4.1. Active state

When the rate of the cathodic process is relatively low (as shown by the solid line in Fig. 3a), the system will be in the active state. The metal or alloy undergoes stable active dissolution at a potential of E_{co} with a current density of i_{co}, and the following conditions prevail:

$$E_0^A < E_{co} < E_{p'} \quad \text{and} \quad i_{cath}(E_p) < i_{cr}$$

The active state is established spontaneously. Hence, if an external perturbation causes the system to move momentarily into the passive potential range, the active state will be spontaneously re-established.

4.2. Active–passive state

For a higher, intermediate rate of the cathodic process (as shown by the solid line in Fig. 3b), there are three possible conditions for the system. These conditions are given at the three points A, B, and C at which the cathodic line and anodic curve intersect.

At potential C ($< E_p$), anodic dissolution of the metal or alloy occurs at a relatively high corrosion rate. At potential B ($\simeq E_p$), the system is in an

unstable state rarely observed in practice. At potential A ($> E_p$), the system is in the passive state, and the corrosion rate is very low. If the system is perturbed, the different conditions of the active–passive state will not be spontaneously re-established.

4.3. Passive state

For a high rate of the cathodic process (as shown by the solid line in Fig. 3c), the anodic and cathodic curves intersect at only one point. The system is in a stable, passive state. The following conditions prevail:

$$E_0^C > E_p \quad \text{and} \quad i_{cath}(E_p) > i_{cr}$$

The rate of metal or alloy dissolution is very low, and is equal to the passive current density i_p. The passive state is also spontaneously stable, which means that, if the passivity is momentarily disturbed, the passive state will be spontaneously re-established.

This kind of system is typical of cathodically modified chromium, stainless steel, and titanium alloys

Table 1. Approximate exchange current density values for the hydrogen evolution reaction on various metals in 1 M sulphuric acid (after Bockris et al. [13])

Metal	i_0 $(A\,m^{-2})$
Ti	$10^{-4.2}$
Au	$10^{-1.5}$
Rh	$10^{+0.3}$
Ir	$10^{+0.3}$
Pd	$10^{+0.9}$
Pt	$10^{+0.9}$

in non-oxidizing acid environments. The chromium, stainless steel and titanium alloys all have passivation potentials more negative than the evolution potential of hydrogen in acidic media. When a PGM is added to any of these alloys, a large increase in the rate of hydrogen evolution will occur, which is large enough to move the corrosion potential of the cathodically modified alloy in the region of stable passivity. Spontaneous passivation of the alloy will therefore result.

4.4. Transpassive state

For a very high rate of the cathodic process (as shown by the solid line in Fig. 3d), or in highly oxidizing environments, it is possible that $E_0^C > E_{tr}$. At this high potential, the metal or alloy will have a higher rate of dissolution than it will at potentials in the passive range, and considerable corrosion can take place.

A comprehensive study by Stern and Wissenberg [6] on the effect of various PGMs and other noble metals in causing the spontaneous passivation of titanium in boiling dilute sulphuric and hydrochloric acids showed that the increase in corrosion resistance of the titanium depends on the concentration of the PGMs added, and also that alloying additions of as little as 0.1% (by mass) resulted in a pronounced improvement in corrosion resistance. They found that the effect of the various alloying elements in improving the corrosion resistance of an alloy generally decreased in the order

$$Ir > Rh > Ru > Pt > Pd > Os > Au > Re.$$
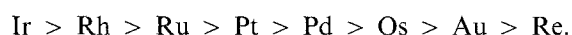
According to available comparable data, there seems to be a reasonable parallel between the hydrogen exchange current densities shown in Table 1 and the extent to which additions of the various PGMs improve corrosion resistance, although a close examination shows that exceptions do occur, and that this agreement is not conclusive.

The relatively high exchange current density of palladium indicates that it should be an effective alloying element in conferring stable passivity. Although equivalent data under these conditions are not available for ruthenium, it is widely considered to be a more effective cathode for hydrogen evolution than is palladium. It should therefore be a fairly effective cathodic modifying agent. Streicher [14] tested palladium, platinum, iridium, osmium, rhodium, and ruthenium as cathodic additives to ferritic stainless steels, and showed that ruthenium additions (0.2%) indeed produced better corrosion resistance than did palladium additions (0.2%). Higginson [15] also confirmed that ruthenium confers better corrosion resistance on ferritic stainless steels than does palladium. The commercial titanium alloy Ti–0.2 Pd containing 0.2% palladium which was developed by the Tomashov group proves that cathodically modified alloys can be economically viable corrosion resistant materials for severe reducing conditions.

5. Mechanism of cathodic modification

Upon formation of the alloy, it is conceivable that the atoms of each alloying component maintain their electrochemical individuality. Consequently, although it is a solid solution, the surface of the alloy is electrochemically heterogeneous at an atomic level, and the atoms of the solid solution do not possess identical corrosion resistance. It seems that the PGMs can inhibit corrosion in two ways, namely:

(a) by acting as a catalyst for hydrogen evolution (and thus increasing the efficiency of the cathodic process); and

(b) by inhibiting the anodic dissolution of the metal or alloy to which they are added.

As a result of the initial interaction of the different atoms of the alloy with the corrosive media, there is a rearrangement of atoms at the alloy surface resulting in a redistribution of the PGM on the surface of the alloy before passivity is established [1, 16].

Three separate mechanisms have been proposed [17] to account for the distribution process, namely:

(i) dissolution of the PGMs, followed by diffusion through the electrolyte and, secondarily, electrochemical deposition of the noble metal on the alloy surface;

(ii) volume diffusion (from the bulk alloy) of the PGM atoms; and

(iii) surface diffusion of the PGM atoms.

The dissolution-deposition model was proposed in some early research into the cathodic modification of titanium alloys [12]. Diffusion of the PGM ions (or complexes) through the electrolyte to the surface of the alloy could easily occur at a sufficient rate to account for the observed redistribution. However, it is impossible for the PGMs to be oxidized in the potential range associated with the dissolution of the cathodically modified alloy, and this fact is a major obstacle, providing a fundamental objection to this mechanism.

The volume-diffusion and surface-diffusion mechanisms do not involve dissolution of the PGM, although the latter model does not preclude the possibility of partial solvation of PGM atoms. However, the difficulty initially associated with these mechanisms was that the diffusion rates associated with similar processes were not high enough to account for the redistribution of PGM atoms at relatively low temperatures. This objection remains valid for the volume-diffusion mechanism.

The important feature of the surface-diffusion mechanism concerns the nature of the surface undergoing anodic dissolution. In recent years, an increasing amount of evidence has emerged which favours the surface-diffusion mechanism in alloying systems that undergo selective dissolution. Forty and Durkin [18] showed that, for silver alloys containing 10 atomic percent gold, the surface diffusion of the more noble component of the alloy (gold) is responsible for substantial re-ordering of the surface during anodic dissolution in nitric acid. Pickering [19] classified the

polarization curves of alloys in terms of their tendency towards selective dissolution and the surface enrichment of the more noble metal. He also pointed out that the morphology of cathodically modified alloys should be that of a solid planar surface enriched in the noble metal. Work by Tomashov et al. [20, 21] on cathodically modified alloys has also provided evidence in favour of a surface-diffusion mechanism.

A surface undergoing anodic dissolution is an extremely disturbed surface because selective dissolution causes a high concentration of defects in the surface. This, in turn, can cause rapid diffusion of the atoms of the noble-metal component to the surface of the alloy. Diffusion coefficients associated with surface diffusion are normally considerably higher than those for volume diffusion, particularly at ambient temperatures. A diffusion coefficient of 10^{-12} cm^2 s^{-1} [22], which is estimated for chromium atoms from a surface analysis of a ferrochromium alloy undergoing dissolution in a 0.1 M solution of hydrochloric acid, is several orders of magnitude higher than the diffusion coefficients required for volume-bulk diffusion, and proves that the observed redistribution rates in cathodically modified alloys can be accounted for by a surface-diffusion mechanism.

6. Conclusions

(1) Cathodic modification can increase the corrosion resistance of materials in non-oxidizing acids by increasing the potential to a value that is in the passive potential range.

(2) During anodic dissolution, noble-metal atoms are redistributed on the surface of the alloy, probably by a surface-diffusion mechanism.

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