Corrosion control with rare earths

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THE HIGH REACTIVITY of rare earths makes them suitable for controlling the corrosion of other metals. They can be used to: (a) improve high-temperature oxidation resistance of chromium- and alumina- forming alloys, and (b) improve the aqueous corrosion resistance of steels and aluminium alloys. The improved high-temperature oxidation resistance is in the form of decrease in oxidation rate and/or increase in scale adhesion. Rare earths can be added to these alloys in elemental form, as oxide dispersions or applied superficially. The increase in oxidation resistance is due to incorporation of rare earths in the growing scale and formation of fine-grained, adherent chromiuk or alumina. Aqueous corrosion of steels and other aluminium alloys can be controlled with rare earths, which help form conversion-type coatings on the alloy surfaces treated by immersion in rare-earth containing solutions or perform as cationic inhibitors when added to the aqueous environment.

Introduction

The homogeneous group of elements occupying the area from lanthanum to lutetium in group III B of the periodic table are the rare earths (REs). Yttrium and scandium are also included with the REs because of their chemical similarities and common existence in nature. Currently REs are used in a wide range of applications, principally in areas such as metallurgy, glasses, ceramics, illumination, electronics, chemicals, and magnets. In recent years, RE elements have found prominence due to increasing focus on various kinds of permanent magnets, optical storage units, fuel cells and high-temperature super-conductors.

The chemical reactivity and oxygen affinity of the RE elements make their extraction difficult and the close chemical similarity among them make their separation, one from the other, an exacting task. These same characteristics permit REs to be used in corrosion control: (a) to enhance the high-temperature oxidation resistance of heat-resistant alloys; (b) to enhance low-temperature aqueous corrosion resistance of various alloys; and (c) as aqueous corrosion inhibitors. This paper addresses the role of REs in controlling corrosion in these three contexts.

Rare earths to control high-temperature oxidation

Alloys or metallic coatings used in high-temperature oxidative environments rely for their protection on a continuous and slow-growing oxide scale. Ideally, these scales should be non-volatile, adherent, coherent, stress-free, pore-free, crack-free, and have low defect concentrations for the transport of species. Commonly, three oxides have these capabilities, namely chromium, alumina, and silica. All three are used in practice and the former two, chromiuk and alumina, to a greater extent than the latter. It was shown over 60 years ago that the addition of small quantities of cerium mischmetall as a deoxidizer to the melt of a chromium-containing heater alloy had a significant effect on the lifetime of the heater alloy. The effect was called the rare-earth effect. Now this effect is referred to as the reactive-element effect as certain elements other than REs also give rise to similar effects. The improvements in oxidation resistance are primarily in the

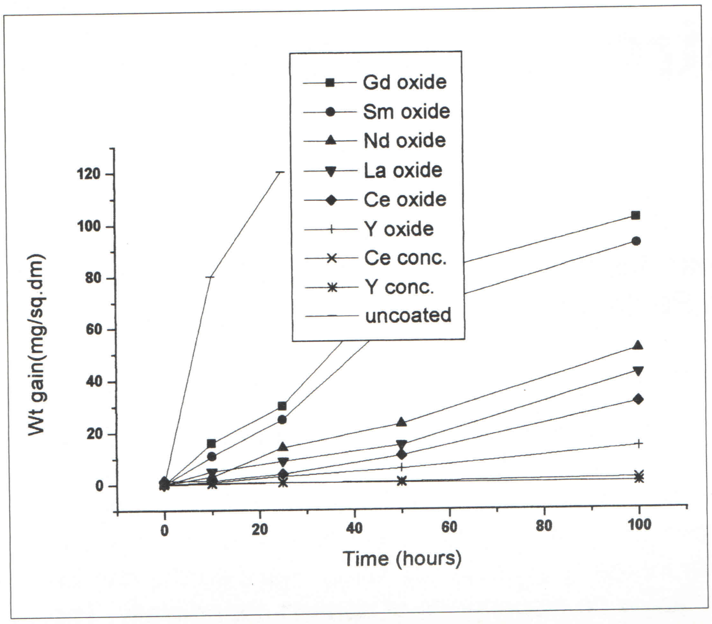


Fig.1. Isothermal oxidation behaviour of AISI 304 uncoated and coated with RE oxides and oxidized at 1000°C.

form of reduced oxidation rates and increased scale adhesion. In various investigations carried out subsequently to study the effect, the REs have been added either to the alloy in elemental form or as an oxide dispersion or applied to the alloy surface.

Addition of rare earths in elemental form

The extent to which REs influence oxidation behaviour of chromium- and alumina-forming alloys are different. In chromium formers, the RE element reduces the amount of chromium required in the alloy to form a protective chromium scale. The amount of chromium required in iron, cobalt and nickel binary alloys to form protective scales are very different (typically 20wt% in iron, 25wt% in nickel and 35wt% in cobalt), but the amount required in all the binary alloys in the presence of reactive elements is approximately the same, at 10-13wt%Cr[1]. The addition of RE elements lowers the rate of growth of chromium at temperatures above 900°C and has little effect below this temperature. The direction of growth of scale changes from new scale forming at the oxide/oxygen interface, to new scale forming at the metal/oxide interface.

The amount of reactive element needed to produce the beneficial effect is small, typically less than 1wt%, and sometimes even less. Many reactive elements produce the effect, and the characteristics of the effect, once produced, appear to be the same. The minimum amount required to produce the effect differs from element to element. Amounts over 1wt% generally lead to a deterioration in the scale adhesion.

The life of alumina-forming alloys is also limited by scale spallation. The addition of reactive elements greatly improves the spalling resistance of alumina scales. Alumina-scale formation is not as dependent on the aluminium content of the alloy as the chromium formation is on the Cr content of Cr-containing alloys, and new scale forms predominantly at the metal/oxide interface, both in RE-free and RE-containing alloys. In recent years yttrium has become the most-commonly used of the reactive elements in alumina-forming alloys.

Addition of rare earths as oxide dispersers

The reactive element effect can also be observed in alloys containing a fine dispersion of RE or reactive element oxide, typically 1-2vol%. Dispersion-containing alloys can be developed by adding RE oxides to the alloy melt or by an internal oxidation procedure. A considerable amount of information is available about the influence of oxide dispersers on the oxidation/corrosion resistance of Ni-, Co-, and Fe-based alloys. In the presence of yttria or ceria dispersions in Cr-containing Ni- and Co-based alloys, the oxidation rates decrease and adhesion of chromium to the substrate increases. Among the three types of alloys, improvements in oxidation resistance in the presence of RE dispersions is much more pronounced in Co-based alloys[2]. As in RE-element containing alloys, the scale-forming reaction in RE-dispersion containing alloys also occurs at the metal/oxide interface. The oxidation behaviour of RE-containing Ni-Cr alloys depends on the type of disperser.

Comparison of the effects of the addition of RE in elemental form or as oxide dispersions has been carried out. It was reported that metallic Ce additions were more effective than cerium oxide additions in producing a fine-grained Cr-rich surface oxide on Fe-20Cr-Ce (CeO_2) alloys for a specific Ce content[3].

Also, the thickness and grain size of the surface oxide decreased with increasing alloy Ce or CeO_2 content in the alloy.

The plasticity of the oxide increased with decreasing scale-grain size. Consequently, the ability of the scale to absorb thermal and growth stresses increased and resulted in enhanced adhesion. The influence of Ce or CeO_2 addition was marked, both in the initial and later stages of the oxidation process, affecting oxide nucleation, scale adhesion, and oxide-growth process. The effects of adding Ce or CeO_2 on oxidation behaviour are quite similar, although the extents are different.

Superficial application of rare earths

Application of REs to alloy surfaces is possible by several methods, including alloying, incorporation into the surface layers by ion implantation, or deposition onto metal surfaces as an oxide coating. Application of RE oxides to metallic surfaces can be done by immersion in aqueous RE-nitrate-containing solution, followed by thermal decomposition of the solid nitrate to oxide. Other precursors for RE oxide coatings can be a molten nitrate salt, an oxide slurry, or a colloidal dispersion of hydrous oxide (sol). The sol gel technique has been shown to generate the smallest oxide particles, and it has been used to produce a range of ceramic coatings. Essentially, it is based on the use of sols, which consist of a stable dispersion in a liquid of colloidal units of hydrous oxides or hydroxides ranging in size between 20A and 15m. The sol is applied to a metallic substrate by a suitable technique, such as dipping, spin coating or electrophoresis. On drying, (removing water from between the colloidal units) the sol is transformed to a gel[4].

The influence of applied Ce, La, or Y nitrate converted to oxides, on the oxidation behaviour of Co- and Ni-based alloys at 1000°C in oxygen is minimal for non-chromium forming alloys[2]. The effect on chromium-forming alloys is, however, significant, and varies with the RE element. This behaviour is associated with the tendency of the RE to form small oxide particles on the alloy surface. When these particles are formed effectively, as in the case of La-, Y-, and Ce-oxides, the effects are most dramatic and appear to be similar to those observed when dispersions of reactive-element oxides are present within the alloy.

The influence of superficial application of various RE oxides and mixed RE oxides as concentrates on the isothermal oxidation behaviour of AISI 304 oxidized at 1000°C is shown in Fig.1[5]. Superficial application of RE oxides reduced the extent of oxidation, with Y and Ce resulting in the highest overall oxidation resistance. The Y and Ce concentrates also reduced the extent of oxidation. The limited influence of the concentrates is due to the presence and distribution of other RE elements with limited (or detrimental) influence on alloy oxidation. The oxides of La, Nd, Sm, and Gd influenced oxidation to lesser extents and in decreasing order.

The mechanisms

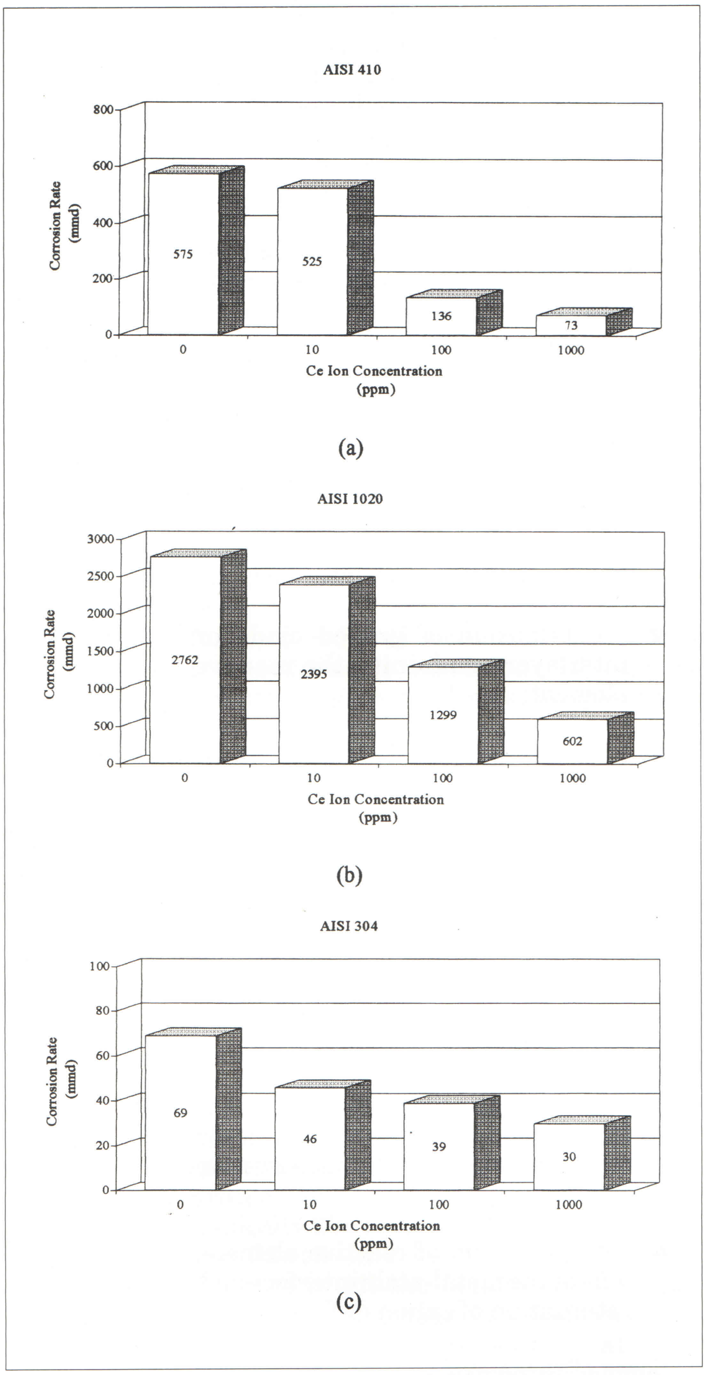
The 'reactive-element effect' has been the subject of many reviews[6-8]. A number of mechanisms have been proposed to explain this effect and include:

- (a) mechanical keying through formation of oxide pegs into the alloy;
- (b) promotion of preferential anionic diffusion rather than cationic diffusion in the scale and thus oxide growth at a different interface;
- (c) formation of graded oxide or interlayers containing the reactive element;
- (d) reduction in accumulation of voids at the alloy-scale interface;
- (e) enhancement of scale plasticity by modification of the structure;
- (f) inhibition of segregation of sulphur at the alloy-scale interface;
- (g) reactive elements acting as scale-nucleation sites;
- (h) modification of microstructure of the scale, and consequently ionic diffusion velocity and oxide stresses; and
- (i) segregation of reactive element ions at the metal-scale interface and retardation of cation diffusion.

Some of these explanations have been verified for specific alloys to which specific reactive elements have been added under specific conditions.

Rare earths to control high-temperature sulphidation

High-temperature sulphur-bearing environments have assumed increasing importance in recent years. In general, the rate of sulphidation of common metals and alloys are four or five times higher than their oxidation rates. This is mainly attributed to the nature of the sulphide scale, which is non-adherent and highly



(a)

(b)

(c)

Fig.2. Corrosion rates of (a) AISI 410, (b) AISI 1020 and (c) AISI 304 steels in 0.1N NaCl with 0, 10, 100 and 1000ppm Ce ions.

porous in nature, whereas the oxide scale is compact and has good adherence with the substrate. Secondly, the metal sulphides have low melting points and also form eutectics with low melting points. The presence of the liquid phase in the growing scale destroys the protective properties of the scale. In the presence of REs, significant improvements in sulphidation resistance at elevated temperatures have been observed. Fe-15Cr-4Al alloys which exhibit high oxidation resistance have low sulphidation resistance. Upon exposure to H_2-H_2S environments at 850°C, these alloys form thick, porous and non-protective sulphide scales. The incorporation of 1%Y in this alloy increases its sulphidation resistance and adherency of the sulphide scale. The increased resistance to sulphidation in the presence of Y is due to the formation of a higher amount of aluminium and chromium sulphides in the inner sulphide scale[9].

Rare earths as inhibitors of aqueous corrosion

Inhibition of aqueous corrosion is achieved if the rates of the anodic and/or cathodic reactions or any of the partial reactions involved in them can be decreased. Many of the inhibitors on which attention has been focussed are anionic inhibitors which function either by favouring passivation of the metal or by forming a protective physical barrier. Development of cationic inhibitors, especially for steels, led to investigation of metal cations which form insoluble hydroxides. A range of metals were investigated and included Ca, Sr, Ba, Cd, and Mn. Cerium which forms insoluble oxides and hydroxides has been shown to act as a cationic inhibitor of corrosion of mild steel and aluminium[10].

Other RE elements also have inhibiting properties. An additional advantage of the REs is their non-toxicity compared to chromates. In the early investigations, in which the inhibitive behaviour of cerous chloride additions to NaCl on Al alloy corrosion was studied, the improvement in corrosion resistance was attributed to the formation of a compact film of cerium oxide[11]. It was later shown that the cerium oxide/hydroxide film formed at local cathodic sites on the surface. The alkaline conditions generated by the cathodic oxygen reduction reaction caused aluminium oxide to dissolve and the cerium oxide to precipitate. The inhibiting effect of other RE elements such as La, Y, Pr, Nd in the form of their chlorides on the corrosion behaviour of high-strength Al alloy AA7075 in NaCl was also verified[12]. Electrochemical polarization tests showed that in the presence of these RE ions, the pitting potential Ep remained the same whereas the corrosion potential Ecorr shifted to more cathodic values. This indicated suppression of the oxygen reduction reaction and reaffirmation of the cathodic nature of inhibition.

The effect of adding varying concentrations of RE chlorides as inhibitors to 0.1N NaCl on the constant and alternate immersion behaviour of Al alloys showed significant reductions in corrosion rate under both types of test conditions[13]. In the constant immersion test, the inhibition effect saturated at 100ppm of RE chloride and the corrosion rate was reported to be almost an order of magnitude below that in RE-free 0.1M NaCl. The stress corrosion cracking resistance as well as the crevice corrosion resistance of high-strength aluminium alloys was also shown to increase in the presence of Ce ions in NaCl solutions.

The corrosion of mild steel in ordinary tap water is also inhibited by cerium chloride additions, and was shown to be due to the formation of a film on the steel surface[14].

In prolonged immersion tests, where mild steel and stainless steels were exposed to 0.1N NaCl containing 0, 10, 100, 1000ppm of Ce ions, the strong inhibiting nature of cerium was shown (Fig.2)[15]. The effect of adding 100ppm of various RE ions to NaCl on the corrosion rate of AISI 304 is shown in Fig.3. These data indicate the corrosion-inhibition potential of rare earths in general.

Besides incorporation into, and formation of, cerium oxide/hydroxide films, the nature of the oxide formed in terms of grain size and morphology also varies.

Rare earths as conversion coatings

Protection of steels and aluminium alloys with conversion coatings is another widely-used form of corrosion control. The conventional procedure for forming conversion coatings on metallic surfaces is through exposure to a chemical agent with which the alloy reacts and forms a protective coating. The use of phosphate and chromate conversion coatings on steels and Al alloys is well known. It is also well known that chromates are both highly toxic and carcinogenic. Therefore non-toxic alternatives to chromates have been sought.

In the previous section on RE inhibitors, it was seen that RE ions inhibit aqueous corrosion of a variety of metals and alloys by forming protective RE oxide/hydroxide film. Based on this, RE conversion coatings were developed.

Upon immersion of an Al alloy in an aqueous solution containing 1000ppm of cerium chloride, hydrated cerium oxide coating forms on the aluminium surface and provides significant corrosion protection in NaCl solution[11]. The degree of protection increases with time of immersion in cerium chloride. Conversion coatings on Al surfaces can also be produced electrolytically by polarizing the alloy in a cerium chloride solution. The cerium coatings produced electrolytically form rapidly, but the extent of protection provided is significantly lower than that provided by the cerium coating obtained by prolonged immersion in cerium chloride solution.

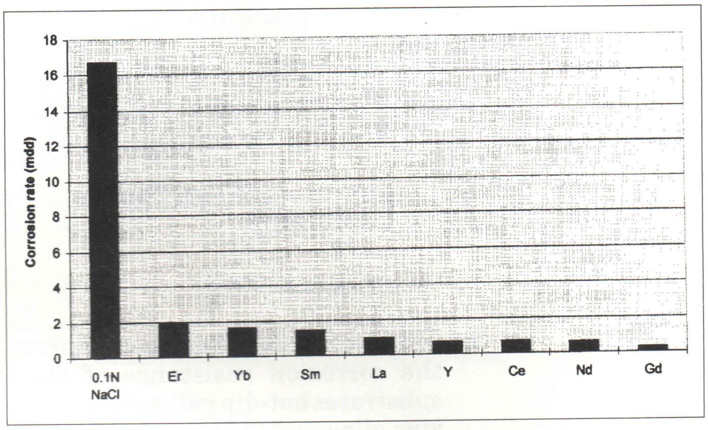


Fig.3. Corrosion rate of AISI 304 in 0.1N NaCl without and with 100ppm rare-earth ions.

Coatings produced by electrodeposition from a solution of cerium nitrate in an organic solvent have also been reported to be defect-free, and were produced in a short time compared to those produced by prolonged immersion[16]. A patented process called 'cerating', which is rapid, involves simple immersion of a metal substrate in an aqueous solution of a cerium salt, an oxidizing agent and various organic additives. A range of metals including Al, Zn, galvanized steel, steel, Cd, and Mg have been successfully coated with this process.

An improved cerate process, which includes a silicate sealing process has been presented[17]. In this process the silicate forms a barrier layer on top of the cerium oxide.

The cerate conversion coating formed by these processes consists of a mixed cerium-aluminium hydrated oxide. According to the mechanism proposed for the formation of cerium oxide films on Al alloys exposed to cerium-containing solutions, the pH at the cathodic sites over the alloy surface increases as a result of cathodic oxygen reduction or hydrogen evolution. When the pH reaches a level at which the solubility product of the hydrated cerium oxide is exceeded, the cerium oxide precipitates. Subsequently, coalescence of the isolated cerium oxide islands takes place forming a coating[17].

Improvements in crevice corrosion resistance of stainless steels exposed to hot cerium nitrate solution has also been reported. The increased corrosion resistance was attributed to chromium enrichment of the surface film formed during exposure to cerium nitrate[18].

Other uses of rare earths to control corrosion

Rare earths have been:

- added to zinc-based alloys to improve the corrosion resistance of steel substrates hot-dip galvanized in the zinc alloy melt[19];
- used to increase the weathering-corrosion (atmospheric-corrosion) resistance of steels[20];
- added to self-lubricating coatings to act as a corrosion inhibitor of metallic surfaces[21];
- added to high-temperature gaseous environments in the form of additives to fuel oil to reduce the incidence of hot salt corrosion[22];
- added to paint systems indirectly - RE cations are adsorbed onto silica or alumina particles to be added as pigments to paints - the water diffusing through the paint releases the RE cations for inhibiting the corrosion of the substrate[23].

Concluding remarks

Rare earths can be used to control high-temperature oxidation and sulphidation, and aqueous corrosion, of various metals. The oxidation resistance of both chromium- and alumina-forming alloys increase in the presence of small quantities of RE added to the alloy, either in elemental form, or as an oxide dispersion, or when applied superficially. The improvements are due to formation of fine-grained, adherent chromium or alumina films.

Aqueous corrosion of a variety of metals such as steels, galvanized steel, aluminium-based alloys, etc., can be inhibited with RE ions. These ions perform as cationic inhibitors and form a compact RE film on the substrate. The cerium ion is a non-toxic inhibitor compared to some well-known chromates.

The aqueous corrosion resistance of steels and aluminium alloys can also be increased with RE conversion coatings. The conversion coatings on Al alloys consist of a mixed RE-Al film and can be obtained by various techniques.

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