Recent developments in corrosion resistant non-ferrous metals and alloys

S. S. MISRA and T. L. RAMA CHAR

SYNOPSIS

The developments during the last two years in the field of corrosion resistant non-ferrous metals and alloys have been reviewed with reference to : materials, environment, properties, applications and future trends. They cover broadly—nickel, aluminium, copper, magnesium, titanium, tantalum, zirconium, beryllium, noble and uncommon metals and others.

THE importance of iron and its alloys as materials of construction has prompted the classification for metals and alloys as ferrous and non-ferrous; the latter includes all the metals (and their alloys) other than iron. However, iron is basically a rather reactive metal and, except in the passive state, is not suitable for corrosion resistant applications. The non-ferrous metals and alloys have established themselves for this purpose, both as protective coatings for iron or as primary materials of construction in corrosive environments. However, these metals are widely divergent in their chemical and physical properties and a common discussion of their corrosion characteristics is rather difficult.

The mechanism of the corrosion reaction is now relatively well understood and the parameters of importance are : physical, chemical, electro-chemical, thermodynamic and metallurgical. The interaction of a metal or alloy with its non-metallic environment results in corrosion. Since metals and alloys are electronic conductors and are built up of cations and electrons that are more or less easily dissociable, and since many environments contain or produce in contact with the metal lattice, ionically conducting species, most corrosion reactions are electro-chemical. The basic kinetic principles have been recently discussed.[1,2] Corrosion resistance (or prevention) clearly depends on the control of the reaction rates at discrete sites on a surface giving rise to anodic currents. As would be expected, these reaction rates are highly dependent upon the nature of the environment, surface and metallurgical factors, and predictions are hard to succeed. Corrosion control, therefore, remains largely empirical.

High purity metals would be quite corrosion resistant, but they lack the strength which impurities impart. Also the cost of producing extremely pure metals would naturally exclude them from being considered for most applications except where cost is of no consideration. One is thus faced with the necessity to devise ways to make these impure metals corrosion resistant, and a common and effective method is by alloying. It is not surprising, therefore, to find the bulk of the recent research and development efforts in non-ferrous metals devoted to the search for newer and better alloys to meet the space-age and other needs. This paper reviews the significant developments in this field from 1966.

Mr S. S. Misra and Dr T. L. Rama Char, Indian Institute of Science, Bangalore.

Environmental factors

The eight forms of corrosion are thoroughly discussed by Fontana and Greene.[3] These are : uniform attack, galvanic or two-metal corrosion, crevice corrosion, pitting, intergranular corrosion, selective leaching, erosion corrosion and stress corrosion. Environmental factors play an important part in each of these.

High temperature

The development of the aerospace industry and the nuclear reactors have prompted the search for alloys suitable for this environment. Chromium by far seems the favourite alloying addition for high temperature oxidation resistance. It is used to improve the well-known nickel and cobalt-base super-alloys.[4,5] Their use in gas turbine engines has been reviewed,[6] chromium addition being responsible for the increased sulphidation resistance under these conditions.[7,8] Other uncommon materials finding use include tantalum[9,10], niobium[11] and hafnium.[12] A hafnium-titanium alloy has been specifically developed for rocketry.[13] The behaviour of various metals under high temperature has been discussed fundamentally.[14]

The alloys of vanadium[15,16] and zirconium[17,18] find major consideration as nuclear fuel cladding elements. Zirconium, a member of the so-called[19] 'exotic' (reactive) metals, has excellent corrosion resistance and its alloys find many other uses including industrial environments[20] and as pressure tube material for organic coolants.[21]

Marine

This is the other severe environment very much in the limelight. The chloride ion present here is somehow able to start penetration through the passive or protective layers responsible for the corrosion resistance of common materials of construction, and corrosion damage occurs. The current importance of desalination makes it imperative that suitable materials are found. A widely reported alloy for the latter purpose is copper-nickel[22–24], titanium[25] appears to be another. The high performance alloys used in pressure hulls and machinery operating under severe marine environmental conditions have been surveyed.[26]

Chemicals

The corrosion problems faced in the chemical industry have been spotlighted earlier.[27] The materials of construction of importance appears to be still the so called reactive metals which protect themselves with a compact oxide layer. Titanium again appears to be the most promising,[20,28,29] but zirconium[20] and aluminium[30] also may be useful. Tantalum[31] and its alloy with zirconium,[32] and a vanadium-niobium[33] alloy are reported to be best to resist corrosion by strong mineral acids.

The new materials of construction for chemical plants have been reviewed by Livesey.[34] A corrosion chart has been published[35] as a supplement to 'Chemical Processing,' and lists the corrosion resistance of the more commonly used materials of construction in 135 different chemicals at 20, 60 and 100°C.

Others

No other environment in particular seems to have attracted the attention of many workers during the period under review. Corrosion in tropical waters have, however, been of some concern. The results of 16 years' test on copper and wrought copper alloys[36] have shown that 5 per cent aluminium-bronze has the best overall corrosion resistance. The corrosion behaviour of aluminium tubing in tropical waters[37] shows that no pitting is observed beyond the cladding for clad alloys, when a potential difference of 0·1–0·15v is achieved between the clad and the core.

Erosion-corrosion and particularly cavitation has attracted some attention. The proceedings of a symposium[38] on the former have been recently published. Cavitation corrosion, a consequence of high velocity flow, has also received attention in another symposium.[39] Aluminium-bronze appears to be a resistant material,[40,41] while small addition of beryllium[42] is reported to improve this property.

Stress corrosion

The corrosion and ultimate cracking of materials under stress has received considerable attention in recent years. Confusion seems to exist, since little useful generalizations have been made, and any prediction still appears to be based on specific tests. A special publication[43] by the American Society for Testing and Materials covers the subject in contributed articles rather thoroughly. There is a report, among others, on the standardisation of test methods,[44] another on some of the techniques used,[45] and a third on the test environment and duration.[46] A rapid electrolytic test method has been devised[47] for aluminium-magnesium alloys. The bulk of the work in this field appears to be tests on the light metals and alloys in various environments—probably a result of their importance as structural materials in the aerospace industry. Titanium and its alloys[48] seem to be the favourite test materials, and next comes aluminium[49]—in particular the latter's high strength alloys. There are also reports on copper and its alloys[43,50], nickel-base alloys[43,51] and magnesium alloys.[52] The book by Logan[53] is a useful contribution to this subject.

Fatigue corrosion, or the failure of metals under repeated stress in different gaseous environments, is the subject of a recent review.[54]

Materials

Classification

The corrosion resistance of different materials was traditionally linked with their standard electrode potential. The limitations of this approach have now been realised, and the so-called 'galvanic series' based on experimental data has achieved primary importance. The main failure of the former thermo-dynamic approach was that it could not take the rate controlling kinetic factors into consideration. Piontelli[55] has come out with a more rational classification based on the exchange current densities of the anodic and cathodic electrode processes. The corrosion resistance of some of the active or reactive metals (which would be highly unstable thermo-dynamically) can be understood in terms of these kinetic factors and the stifling effect of the compact oxide film formed as a corrosion product on the surface.

Another classification attempts to separate them in terms of density : light and heavy. The light metals such as aluminium, titanium, magnesium and beryllium are of importance to the aerospace industry. All of them come under the 'reactive' category, and a compact protective layer is responsible for their corrosion resistance. Under the 'heavy' class come such common non-ferrous metals as copper, nickel, chromium, zirconium and the noble metals. The resistance mechanism is obviously quite varied in this class.

Effect of alloying

The bulk of the recent research and development efforts have been directed to the search for newer and better alloys, since alloying is an easy way of imparting corrosion resistant properties to a material. This can be done in three different ways : (1) the alloying addition modifies the cathodic processes, (2) it modifies the anodic process, and (3) it helps in the formation of a protective film. A fourth desirable effect of alloying is the dilution of a resistant but expensive parent matrix with a cheaper metal; the latter, of course, should not reduce the corrosion resistance in the process. An example of this is the addition of niobium to the more expensive tantalum.[10] Tomashov and Chernova[56] have discussed the fundamentals of the development of resistant alloys.

General

A bibliography of recent publications on corrosion resistant materials is given in the appendix. A survey of published literature shows that the major materials of concern are the following: copper and copper-base alloys, nickel and nickel-base alloys, aluminium and its alloys and titanium and its alloys; a separate treatment of these systems follows.

Copper and copper-base alloys

The application of these materials is already well established. Copper is a noble metal and its alloys retain this property to a considerable extent. Selective leaching is a problem when the alloying material is active (zinc, aluminium), particularly so if the alloy is a two-phase system.[57-61] The outstanding resistance of copper-nickel alloys in marine environment and its widespread use in desalination equipment has been spotlighted earlier.[22-24] Also mentioned earlier is the superior cavitation resistance property of aluminium-bronze.[40-42] Brass containing phosphorus (up to 5·8 per cent) appears to be more corrosion resistant[62] than ordinary brass. A tarnish resistant copper-aluminium-zinc alloy which can substitute copper for decorative uses has been developed;[63] the resistance is conferred by an invisible aluminium oxide film. A 'stainless' copper,[64] which is basically an aluminium-tin-bronze composition, has high corrosion resistance and does not need a clear lacquer protective coating. A copper alloy with small amounts of zirconium and vanadium is suitable for electrical applications at elevated temperatures.[65]

Nickel and nickel-base alloys

The corrosion resistance of nickel coupled with its aesthetic appeal had established[66] its decorative and protective applications even before the nickel-base super alloys were devised to meet today's severe requirements. There are quite a few of the latter available now, going under such trade names as Hastelloys and Inconels. Their usefulness in marine hot corrosive environment has been already referred to.[4,5,23] A recent review is available[67] on the state of their technology. They are being used in the gas turbine engines[6] where sulphidation[68] appears to be the main problem. It was noted earlier[6-8] that chromium content in the alloy improves this property. Nickel and nickel-base alloys are reported to resist molten caustic soda,[69] hydrofluoric[70] and hydrochloric[71] acids. A heat-treated nickel-titanium alloy[72] containing approximately equal percentages of each constituent may find application in extendable elements such as antenna, reflector, etc. for space-crafts.

Aluminium and its alloys

These members of the light metals category are of extensive use as materials of construction, and new developments have been recently discussed.[73] Their importance in the aerospace[74-77] industry has naturallyled to a multitude of studies on the stress corrosion aspects in various environments.[44,47,49,78,79] Aluminium alloys are also suitable for marine applications[23,24]—particularly the aluminium-magnesium-type,[80] the intergranular corrosion in the latter may be improved by the addition of manganese.[81] Alloying with silicon, iron and magnesium may be desirable for resistance to alkaline building materials.[82,83] A new technique of pressurized plastic sheathing[84] may make the already established[85,86] use of aluminium cables suitable for underground installation.

Titanium and its alloys

They are relatively new entrants to the field, the first commercial application being in 1952. The deterrent was the high cost of production, although titanium ores are even more abundant than those of iron. However, the desirable corrosion resistance properties are responsible for the steady and rapid rise in their use in recent times. Titanium is thermo-dynamically active, but the resistance is imparted by a compact protective oxide film which even chloride ion does not penetrate at room temperatures.[87,89] Some recent reviews on their suitability have been mentioned earlier.[19,66,73] Their importance in marine environment[23,25,57] has prompted the development of a few newer alloy compositions.[90,91] Comparative test data on their performance in this medium are available.[92,93] The other severe environment where they find consideration is chemical[29,94] and industrial.[20,28] Several publications report their performance in inorganic acids and chlorides, and on their stress corrosion cracking behaviour in various environments.[43,27,95,96] A new stress corrosion resistant alloy is claimed to have been developed.[97]

Others

Apart from the four systems discussed above, a number of others find consideration during this period. Most of them are rare metals and their alloys and have been specifically developed to meet particular uses. They have been referred to earlier under environmental conditions such as high temperature or chemicals. Some like chromium[4-6], niobium[11,12,33], molybdenum[51] and tungsten[9,69] also find wide mention as favourable alloying additions to impart resistance. Others like magnesium[25,52,66-73] and beryllium[25,42,73] are considered because of their favourable strength-to-weight ratio. Of importance purely because of their superior corrosion resistance are tantalum[9,10,31,32,49] and hafnium.[12,13] Vanadium alloys find use mainly as cladding materials in nuclear reactors,[15,16] and have good resistance to minerals acids.[33]

Noble metals find various applications in industry.[98]

Zirconium and its alloys

This 'exotic' metal[49] and its alloys find application in nuclear reactors as fuel cladding[17,18] and other uses[20,21]; they are corrosion resistant.[32] Coins made of a new alloy[99] with 10-12 per cent hafnium may replace those of silver in appearance, metallic ring and resistance to wear and chemical attack.

Cobalt and cobalt-base alloys

Superalloys of cobalt and nickel-base are well known now, and their high temperature corrosion resistance has been mentioned before.[4,5] They resist sulphidation[7,100] and the state of the art for their uses in process metallurgy have been reviewed.[101]

Trends and possibilities

Only very few general trends emerge during the period under review from what is seen so far, although the coverage tends to be representative rather than exhaustive. The rigorous performance requirements of the modern times have spurred interest in the exotic and rare metals, but this can succeed only where cost is of no consideration. Established materials such as nickel-base, copper-base, aluminium and (relatively new) titanium alloys continue to be of major interest. The bulk of the work is on tests on suitability in various environments, and some on the development of new alloy systems. Very little fundamental work on understanding the basic processes is available.

Importance of design

Material limitations being what they are, design assumes considerable importance in corrosion prevention. This aspect has been emphasized by a few publications.[22,102,103] A successful design has to strike a balance between all of the following factors: structural, environmental, economic and aesthetic.

Future possibilities

The current pre-occupation with gathering of actual test data is bound to continue for some time. This is because no fundamental approach, either empirical or semi-rigorous, is available to satisfactorily predict the performance of materials. Great strides are being made in the understanding of simple systems such as pure metals. The kinetic parameters involved in multi-component alloy systems or in stress corrosion cracking are, of course, much more complicated. But the future will probably see a sufficient development in the theory as applicable to these systems, and then a breakthrough would have been achieved in materials development.

Situation in India

The awakening of the rest of the world to the importance of corrosion research has been echoed in the Indian scene. The Corrosion Advisory Bureau of the C.S.I.R. holds regular meetings[104] and lists of papers published by Indian authors appear periodically.[105] The non-ferrous metals industry in India has been discussed by Nijhawan.[106] Resources for most of the common and strategic ones such as copper, zinc, cadmium, nickel, lead, tin and cobalt, are either inadequate or poor. We do have adequate resources of aluminium, beryllium, chromium, manganese, magnesium, titanium and zirconium. The extremely adverse balance of payment position has focussed attention on the substitution of scarce non-ferrous metals,[107-109] and aluminium may be able to replace copper, lead, tin, zinc and nickel for many applications. Titanium is conspicuously absent, in spite of its world-wide importance and seemingly favourable properties. Abundant resources of this material are available and economic production could enable it to replace stainless steels or nickel-base superalloys in many applications. Development of new materials consistent with the available resources and evaluation of their performance under the conditions prevailing in practice, will go a long way in meeting the corrosion problems faced by the Indian industry.

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