



Corrosion Resistance of the Austenitic Stainless Steels in Chemical Environments

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Abstract

The quantitative data secured in corrosion tests are often of a very low order of magnitude. When the corrosion rate is of the order of less than 0.1 mils penetration per year, the actual numbers carry little significance. If, for example, a test indicates a corrosion rate of 0.1 mils penetration per year for Steel A, and .002 for Steel B, it should not be concluded that Steel A is twice as good as Steel B, but rather that both steels are entirely suitable for service in the environment.

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INTRODUCTION

In many instances, the desirable physical and mechanical properties of austenitic stainless steels may determine their use, but it is generally true that their most important property is their ability to withstand corrosion in a great many of the environments likely to be encountered by modern materials of construction[1]. The stainless steels possess an especially useful characteristic in resisting corrosion in that they perform best under those oxidizing conditions which are most harmful to ordinary steel and to many of the non-ferrous metals and alloys[2]. It is also highly significant that the stainless steels demonstrate practically complete resistance to the corrosive effects of the most commonly encountered environment—the atmosphere[3]. Not only do they resist structural damage in atmospheric exposure, but in addition, and in line with their descriptive name, they retain their original bright appearance for long periods[4]. Cold forming operations and cold rolling generally do not decrease the corrosion resistance[5].

The alloys are, of course, not impervious to corrosion in all environments. With respect to certain media, corrosion of different types may occur. The extent can often be minimized by proper composition selection and careful conditioning. When held in the temperature range between 800 and 1650 F, the

austenitic stainless steels may undergo a change which renders them susceptible to intergranular corrosion upon exposure to a number of corrodents, including some which otherwise may have slight effect on them[6]. In this temperature range chromium carbides precipitate in the grain boundaries. The resultant areas of lowered chromium content adjacent to the grain boundaries have less resistance to corrosion[7]. Welding operations, for example, may leave an area near the welds in such a corrosion-susceptible or “sensitized” condition. The intergranular corrosion of a sensitized steel can be insidious, in that after such attack the steel sometimes appears relatively sound, but on more detailed examination may be found to possess very little strength. A steel which has been sensitized (either by heat treatment or by welding) will be seriously subject to intergranular corrosion only in certain specific environments[8]. The original high corrosion resistance of the chromiumnickel austenitic stainless steels can be restored after sensitizing thermal exposure provided they have not been exposed to an effective corrodent in the meantime. Simple annealing by heating to 1850 to 2050 F followed by rapid cooling through the sensitive range is sufficient for the purpose. Increasing carbon content tends to increase susceptibility to sensitization [9].



Holding the carbon content to a maximum of .03 per cent, as in Types 304L and 316L, is sufficient to avoid sensitization during welding and stress relief annealing, but a further reduction to 0.02 per cent maximum is required if there is to be continued operation in the sensitizing temperature range'. Additions of titanium or columbium also serve to inhibit the development of sensitization. These elements form carbides more readily than chromium and thus diminish depletion of the latter along grain boundaries. Therefore, if the low carbon grades are not used, Types 321 and 347 are recommended for use in corrosive environments which may cause intergranular attack where welded construction is employed and annealing is not practical. Titanium is reactive with gases at welding temperatures so that it is partially lost during welding. Type 347, containing the less reactive columbium, is usually employed for weld rods in such applications. An extensive discussion of the effects of steel composition, thermal treatment, and evaluation test procedures has been published by ASTM.

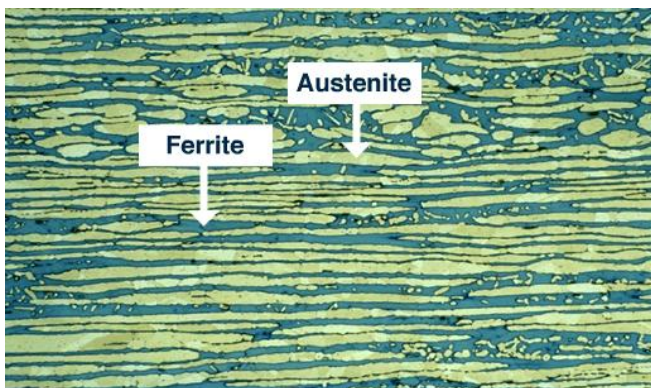


Figure 1. Stainless steels have a two-phase microstructure of austenite and ferrite grains.

A thorough compilation of case histories of stress corrosion cracking has been published by the ASTM. Additions of other elements have little value in reducing stress corrosion cracking. To avoid all danger of cracking in those specific environments known to be capable of causing this difficulty, as, for example, those listed in Table II, practically complete elimination of internal stresses, such as those introduced by welding, is necessary [10]. This requires annealing at quite high temperatures. For media such as those listed, the annealing temperatures may need to be in excess of 1600 F. Even so, stresses introduced on cooling can be a problem.

Pitting Corrosion

When passive metals such as the stainless steels corrode, the corrosion develops where passivity has been destroyed. This may occur at very small areas and result in a pitted surface [11]. Once the passivity has been lost at a local spot, this area will be anodic to the remaining passive surface. The subsequent

development of these active anodic areas into pits will depend upon electrolytic current flowing between the small anodic area and the large unattacked cathodic area outside of the pits. Some oxidizing agents serve to depolarize this large cathode area and thus accelerate the rate of pitting. Oxygen in stagnant solutions, ferric chloride, hypochlorous acid, and mercuric chloride are typical oxidizing agents which will promote pitting. On the other hand some oxidizing agents will prevent the activation of local areas on stainless steel and thus prevent corrosion. The nitrates and chromates are good examples of this group. The role of dissolved oxygen in pitting may assume different aspects. In the complete absence of oxygen, or other oxidizing agent, the cathodic areas will not be depolarized and the development of pits will be arrested. If oxygen is present in small amounts, and the corroding solution is stagnant, the passivity may not be preserved over the entire surface and pits may develop. Liberal aeration may in some instances supply a concentration of oxygen which is sufficient to maintain a protective passive film over the entire surface and pits will not develop. Thus good aeration and moderate velocities or turbulence are useful in maintaining adequate oxygen supply; for example, in sulfuric acid, and in sea water and other salt solutions [12].

If debris of any kind is allowed to accumulate on the surfaces of stainless steel equipment, it will reduce the accessibility of oxygen to the covered areas and pits may develop in such locations because of the reduced oxygen concentration. Marine growths such as barnacles, sludge settling to the bottom of tanks, and carbon deposits from heated organic compounds are typical examples of this source of corrosion of stainless steels. Pitting corrosion is rendered less severe by the addition of 2 to 3 per cent of molybdenum to stainless steel. Molybdenum additions also have the specific effect of reducing corrosion of the austenitic stainless steels in certain media such as sulfurous acid, sulfuric acid, phosphoric acid, formic acid, and some other hot organic acids. To maintain the austenitic structure in these molybdenum-containing stainless steels, the nickel content must be increased. Thus Type 316 contains 10 to 14 per cent nickel as compared with 8 to 10 per cent in Type 302.

Crevice Corrosion

In the design of stainless steel equipment, all shapes and joints which form crevices or deep recesses should be avoided. Oxygen does not have ready access to the areas within the crevice and these may become anodic to the remaining exposed, aerated areas of the equipment [13]. The extent of attack within the crevice has been shown to be proportional to the area of the

freely exposed metal outsides. This form of corrosion of stainless steel may be eliminated or reduced to a minimum by completely sealing such crevices, or by altering design to eliminate them. If gaskets are used, they should be non-porous and pulled up tightly over their entire area.

Galvanic Corrosion

When designing equipment to be constructed with several materials, thought must be given to possible galvanic couples. The stainless steels are usually quite cathodic relative to other alloys but their potentials may vary over a wide range depending upon whether they are in an active or passive state. Type 304 stainless steel in sea water has exhibited electrode potentials from $i-0.5$ to -0.28 volt referred to the saturated calomel electrode". The austenitic stainless steels accordingly may be expected to be cathodic to most of the common structural alloys such as ordinary steel and aluminum. This usually will mean a reduction in the normal corrosion rate of stainless steel since it profits from mild cathodic protection. On the other hand the less noble alloy in the equipment will not be excessively attacked if its area is large compared with the area of the stainless steel.

Corrosion of Stainless Steels In Various Environments

As it is obviously not practical to discuss individually the behavior of stainless steels in contact with the thousands of corrosive media and under the variety of conditions which may be encountered, corrosive environments will here be divided into several general classes and the behavior of the austenitic chromium-nickel stainless steels in each of these types of environment summarized with appropriate data to illustrate particular points[14].

Corrosion by Bases

The 18-8 stainless steels have excellent resistance to corrosion by weak bases such as ammonium hydroxide and organic compounds like aniline, pyridine, and the aliphatic amines. Type 304 can be used for such equipment as ammonia stills and for certain types of amination reactions. The performance of stainless steels in solutions of strong bases may be illustrated with results of tests in sodium hydroxide solutions, as summarized in Table XIII. The 18-8 steels usually show very slight attack in solutions up to 50 percent NaOH concentration at temperatures up to about 220 F. In higher concentrations and temperatures corrosion rates are likely to be appreciable. Under conditions of stress, stress corrosion cracking of stainless steels may occur in hot sodium or potassium hydroxide solutions[15]. Hot metal surfaces wetted by dilute solutions

may be so affected due to concentration of the caustic by evaporation.

CONCLUSION

Considerable care must be exercised in the use of stainless steels where halogens are to be encountered. Types 304, 316 or 317 may be used for pipe lines to handle dry chlorine gas at low temperatures but are not suitable for wet chlorine gas or hot chlorine, wet or dry. Severe attack by dry chlorine may be expected at temperatures over 600 F. In some cases, calcium hypochlorite bleaching solutions, containing not more than 0.3 per cent available chlorine, can be safely handled in Type 304 vessels for short periods of time not exceeding four hours, followed by thorough washing with water. However, Types 316 and 317 generally are preferred for this type of service because of superior resistance to pitting. These materials are used to handle alkaline sodium hypochlorite bleaching solutions containing 0.3 per cent available chlorine through entire bleaching cycles.

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