Stainless Steels and Other Ferrous Alloys

WALTER A. LUCE JAMES H. PEACOCK

The efforts to control the susceptibility of stainless steel to localized corrosion, successful application in chemical operations, and high temperature alloy development highlight the technological progress in this field.

The statement, "There is no nickel shortage," is cause for argument in any industry using nickel containing alloys. The chemical industry, being a large user of the Cr-Ni stainless steels, has encountered extended delivery times and perhaps even price increases, both of which have been attributed to the nickel shortage. Though there is no shortage of nickel deposits throughout the world, the supply of refined nickel does not meet the demand. The imbalance between nickel demand and production can be attributable to strikes, labor shortages, and unprecedented demand.

Nickel producers are steadily expanding their facilities resulting in an increased rate of production, but consumption is increasing at an even more rapid rate. The high level of industrial activity, coupled with the Vietnam effort and defense needs in the United States, is responsible for the demand's being so great. Even inventories that have been built up over the years have been depleted during 1966 because demand has outstripped supply. In addition to the producer's inventories, some of the government stockpile has been released for domestic consumption. However, approximately 90% of the government stockpile has gone for defense orders whereas only 10% has gone to alleviate hardship cases in industry. This, in essence, means that very little of the government stockpile was available to produce stainless steel equipment for use in the chemical and allied industries.

It is significant to note that the Free World consumption of nickel in 1966 was estimated at 840 million pounds, or an increase of 80 million pounds over the 1965 record year. Perhaps even more significant is the fact that of this total, 280 million pounds was used in the production of stainless steels. This is the single largest usage of nickel. It is estimated that the consumption of nickel in stainless steels more than exceeds the combined total of the next two highest usage fields of nickel, that is, nickel plating and high nickel alloys. With the high quantity of nickel being used for stainless steels, and with these alloys being used extensively in the chemical industry, it can easily be seen why stainless steel chemical process equipment may be in short supply.

Many producers have considered scrap nickel containing alloys as charge materials for producing stainless steels. Unfortunately, the exorbitant price that must be paid for such scrap in some instances, coupled with other metallics and nonmetallics that may be included in the scrap, either intentionally or unintentionally, has resulted in problems. Hence, producers of stainless steel alloys are becoming ultracautious about using nickel alloy scrap as a charge material to produce stainless steel alloys.

Though the rate of production of nickel in 1967 is expected to be greater than in 1966, the actual consumption may be less because producer's inventories have been depleted. However, the price increase in electrolytic nickel is permitting further exploration of high cost, low grade ore, and it is anticipated that significant increases in production will satisfy the 1968 and long term demand.

CORROSION

There is continued emphasis on research efforts designed to control the susceptibility of stainless steel to localized corrosion. While stress corrosion cracking is still the most insidious and perplexing of the various forms of localized corrosion facing the chemical process industry, there is also continued interest in intergranular corrosion, pitting attack, crevice corrosion, and so forth.

As cited in past reviews (*4A*), the major research emphasis centers on preventing localized breakdown of passive films. The successful application of stainless steels in most chemical environments depends upon these films. One approach is to predict the point at which the film becomes vulnerable to breakdown; a potentiometric approach is being used to determine this point. A potential measurement technique can also be used to determine the relative strength of film a particular alloy can develop in a given environment. On this basis, the consistency of passive films and the reliability of the alloy may be made more predictable to extend the application of an important group of corrosion resisting alloys. Thus, potential studies are being refined to the point where they find wide acceptance in determining the suitability of stainless steels in a variety of test programs.

The influence of various elements on the susceptibility of different stainless alloys to stress corrosion cracking continues to be investigated. Chromium and silicon were found (*2A*) to have a beneficial influence in minimizing the cracking tendency of a normally susceptible alloy while molybdenum had the opposite effect. These particular elements undoubtedly affect the passive film. While dislocations are still felt to be the logical primary sites for crack propagation, a strong film may bridge these susceptible areas. Once a thorough understanding of the true influence of various elements on stress corrosion cracking develops, a balanced composition may very well allow relatively standard alloys to resist this perplexing form of attack.

Further work is also needed on the influence of certain critical trace elements on crack susceptibility. Ultrahigh purity stainless steels have been melted as an aid in evaluating the influence of contaminants. The various trace elements can be added selectively or in combinations to determine their influence on a base composition (*5A*).

Until research provides new alloys with improved stress corrosion resistance, the most useful approach will be to test standard alloys in the various environments and determine the degree of resistance under varying stress by potentiometric means. These potential studies will provide a good indication of the suitability of various alloys to this form of attack.

Cold work also has a known deleterious effect on the resistance of the austenitic stainless steels to stress corrosion cracking. This fact helps emphasize that every possible precaution must be taken by fabricators of chemical processing equipment to minimize residual stresses during fabrication. When stressing is unavoidable, good stress relieving practices should be followed to reduce problems.

Some attention is still being given to intergranular corrosion since failures of equipment occur in practice with a surprising degree of regularity. Aust (*1A*) and others discussed a situation of preferential grain boundary attack in certain stainless steels which had a seemingly suitable solution annealing treatment prior to exposure. This situation was attributed to variances in composition between the grains and grain boundaries during solidification; such variances can best be prevented by a more thorough heat treatment than normal. It is well known that care must be exercised in the processing of stainless steels to assure homogeneity, but slight differences in the microstructure may be exploited under specialized conditions. Potential studies are also being used to evaluate the susceptibility of stainless alloys to intergranular attack.

Potential studies are being used to determine when an alloy is susceptible to pitting corrosion (*3A*). This form of attack is still receiving attention because stainless steels still pit in the presence of chlorides. Pitting attack is also one of the most insidious forms of failure because, with a surprisingly low loss of metal, equipment can be rendered completely unsuitable for further service.

AUTHORS *Walter A. Luce is Technical Director and James H. Peacock is Manager, Materials Engineering with Duriron Co., Dayton, Ohio. They have presented the I&EC's annual review of progress in this field since 1951.*

Research efforts are now in progress to develop alloys that will withstand temperatures up to 2300°F to meet the severe demands of industry

INDUSTRIAL APPLICATIONS

Detailed information of the successful application of stainless steels in chemical operations is contained in the literature each year. Such data normally indicate where these important alloys can be applied, providing no metallurgical or fabrication deficiencies exist to make them susceptible to the various forms of selective corrosion discussed above. One report (*3B*) provided detailed information on the resistance of nickel containing alloys, including stainless steels, to phosphoric acid.

The use of polarization-resistance studies as a means for screening alloys for application in severe chemical environments was discussed by Butler and Carter (*1B*). The technique of utilizing potential measurements to determine the general acceptability of alloys is also gaining wide acceptance. It not only detects susceptibility to selective attack, but indicates the general acceptance of the material in a complex environment which may take months to evaluate by more conventional testing. However, prior history of the material is vitally important in the correct interpretation of data obtained, since improperly processed material may indicate general unacceptability of an alloy which may actually be resistant.

The influence of contaminating corrosives is also being studied because they can often influence the suitability of a material in a particular environment. Hydrogen sulfide and sulfur dioxide are known to have a deleterious influence on the resistance of certain stainless alloys to sulfuric acid. Potential studies reported by Herbsleb and Schwenk (*2B*) verified that the presence of these compounds can change the basic resistance of stainless alloys. Thus it is possible to determine whether a contaminant will alter the resistance of a particular alloy to corrosive conditions, and if so, determine how much can be tolerated.

Cryogenic applications continue to receive attention largely because our space effort makes it mandatory to have detailed knowledge on how low temperature influences various alloys. The stainless alloys are particularly important because of their general stability at low temperatures, but additional information is needed on the importance of the many variables including composition, defects, etc., to allow designs to be made to extremely close tolerances. Much of this information will ultimately be useful to the chemical industry by permitting more economic designs to be adapted to their cryogenic applications.

HIGH TEMPERATURE

There is continued emphasis on high temperature alloys since operating conditions are continuing to get more severe. Thus, design engineers are requiring more data to increase the reliability of their material selections but in many cases, these data are not available. Simmons and Van Echo (*2C*) provide considerable data on various cast and wrought stainless steels which are commonly used under elevated temperature conditions. This publication is an excellent summary of available information.

In recent years the corrosion grades of stainless steels are receiving increased emphasis for elevated temperature applications but data are restricted to approximately 1600° F. maximum because of strength problems. However, work continues on these alloys to further understanding for future possibilities. Deleterious metallurgical reactions which restrict the serviceability of these alloys may be eliminated by a better understanding of the materials, such that their serviceability will ultimately be extended.

Alloys are required to handle conditions in the 2000° to 2200° F. range, and research efforts are now in progress to raise the upper limit to 2300° F. Puyear and Silence (*1C*) describe their work on various alloys in contact with superheated steam in the 2000° and 2200° F. range. On the basis of their tests, attack by steam is similar to that occurring in air which suggests that a knowledge of oxidation behavior in air can prove useful in selecting alloys for high temperature service in steam. Considerable work will be necessary in the next few years to obtain alloys with suitable high temperature properties to meet the severe demands of this industry.

ALLOY DEVELOPMENT

Economy is of importance to every industry but the adaptation of stainless steels to the chemical industry depends on both economy and metal characteristics. The same may not be true in the space industry because special metal characteristics are of prime importance, and

Considerable emphasis centers on improving the strength and ductility of existing alloys as well as exploring specific applications

economy is of secondary interest. This undoubtedly accounts for so much emphasis on the mechanical properties of the PH (precipitation hardening) stainless alloys and so little emphasis on the corrosion resistance. Nevertheless, for any of the newer, or revised older stainless alloys, to become prominent in the chemical industry, economy must be rated at least as important as metal characteristics.

In the economy category are initial cost, life expectancy, installation costs, maintenance requirements, and availability of service in case of emergency. Under metal characteristics would fall production techniques, heat treatment, fabrication, machining, mechanical properties, physical properties, chemistry, and corrosion resistance. The last item is of extreme importance because the high temperatures and pressures, combined with the aggressiveness of many process solutions, demand a thorough knowledge of the corrosion resistance of a given alloy. Furthermore, most aspects of the economy of a given alloy are directly related to corrosion resistance.

The PH stainless steels continue to follow the trend of recent years. Considerable emphasis centers on improving the strength and ductility of existing alloys as well as exploring specific applications. The outstanding mechanical properties being achieved are, in many instances, beyond expectations. Though these PH alloys are neither noted nor exploited for corrosion resistance, the basic constituents in many of them indicate their potential use in corrosive environs. For instance, it would seem logical to explore fully the stress corrosion cracking resistance of these alloys to establish whether they offer any advantage over the older, more prominent stainless alloys.

Boron is a beneficial addition to a Ni-Cr-Mo-Ti PH stainless steel. Distributing the precipitate in the hardening treatment permits higher titanium contents resulting in higher strengths without adverse effects on ductility. In the interest of lowest possible weight combined with highest possible mechanical properties, another PH alloy was developed with Cr, Ni, and Co as the major constituents. Complex heat treatments are often required to achieve the ultimate combination of strength and ductility. If and when detailed corrosion studies are conducted on the various PH alloys, special emphasis will have to be given to the carbon content and heat treatment because these are two very critical aspects of stainless alloys.

Interest in the maraging steels has led to a study (*5D*) of a low carbon, 12% Cr-8% Ni, beryllium containing maraging stainless steel. Reports that such alloys could be age hardened to in excess of 600 Brinell prompted the study, and the initial results proved encouraging. The tensile and impact properties were of sufficient interest to warrant additional work to establish the optimum beryllium level and heat treatment. Inclusion of corrosion data in such studies would be a worthwhile contribution. The same is true of another relatively new Cr-Ni austenitic stainless steel (*3D*) possessing a yield strength in the magnitude of 250,000 to 300,000 p.s.i.

Stainless steels have always been popular materials of construction for cryogenic applications but long time creep of bolting materials has created some problems. The recent development of a low carbon, chromium-nickel stainless steel containing more than 0.1% nitrogen exhibits high resistance to creep. This of course minimizes any tendency for the bolt to slacken as the result of creep and consequently permits maintaining a tight joint. Equally important can be the savings and safety achieved by avoiding loss of product.

In the field of castings, the Alloy Casting Institute (ACI) alloy CD-4MCu is continuing to show great promise in the chemical industry. It has outperformed the straight Cr, Cr-Ni, and Cr-Ni-Mo stainless steels in nitric acid applications containing other constituents; in various phosphoric acid services with and without solids; and in organic as well as salt solutions. The broad scope of its complete applicability is unknown, but evidence thus far indicates this 25% Cr, 5% Ni, 2% Mo, and 3% Cu alloy will have widespread application in the chemical industry. However, close production control techniques must be exercised, particularly with respect to chemistry and heat treatment, if optimum properties and corrosion resistance are to be achieved. It is unfortunate that this two-phase, austenitic-ferritic alloy cannot be produced in wrought form, because its outstanding combination of properties and corrosion resistance would undoubtedly mean demand for large tonnages of the wrought alloy.

MANUFACTURING AND FABRICATION

As is generally the case, welding is in the forefront in the manufacture and fabrication of stainless steels. It is particularly important to the chemical and allied industries because they require strong, sound, crack free weldments. In addition, the resulting fabrication must possess corrosion resistance at least equivalent to the base metal before the welding operation. The combination of these characteristics is cause for much concern year after year.

Much has been written and reported in the past pertaining to the influence of phosphorus and sulfur on hot crack susceptibility, mechanical properties, and corrosion resistance of weld metal in austenitic stainless steels. However, it is noted that there is a lack of detailed information on the maximum amount of phosphorus and sulfur that can be tolerated. Recent work by Bernstein and others (*1D*) points out that sulfur has a much greater influence on mechanical properties than phosphorus, and austenitic filler metals should be limited to 0.015% sulfur maximum for critical applications. The present phosphorus limit of 0.03% maximum for the low ferrite containing metals appears to be adequate. This report also considers the relationship of high temperature ductility and hot cracking sensitivity, room temperature ductility, and room temperature impact strength.

Cracking of fully austenitic weldments has been a problem, and recent data indicate that introducing carbon as a deoxidizer into the weld metal, via the coating, prevents this type of crack. This results in a higher carbon content in the weldment which may affect the corrosion resistance in certain critical media. Crack-free corrosion resistant weldments are also claimed to be attainable by lowering the silicon content of the weld metal as compared to the base metal. Exceptional corrosion resistance of the weld is achieved by creating a galvanic couple with the base metal; the weld metal is the cathode. The large ratio of anode (base metal) to cathode (weld metal) has an insignificant effect on general corrosion of the base alloy.

Fabrication of cast stainless steel components into relatively complicated large castings, as well as weld repair of castings, is gaining increased acceptance. Present welding technology and past experience, when properly combined and exercised, permit an end product that is at least as good as a casting free of weldments. It is entirely conceivable that a given stainless steel casting could be made more economical, with better quality, by utilizing welding. No longer is there any foundation to the theory that corrosion resistant stainless steel castings should not be welded. By realizing that any weldment should be equal to or better than the base metal in all aspects, including corrosion resistance, and by taking the necessary precautions to assure this, a more desirable product can result. In reality, weldments of any length, width, and depth on stainless steel castings could be made and not impair the serviceability of the casting in the slightest. Nondestructive testing techniques can provide further assurance of the integrity of the casting.

Because of the basic necessity of overdesigning stainless steel castings, stress relief seldom becomes a critical factor. With wrought stainless equipment, many media will exploit highly stressed areas, thus establishing the need for stress relief. It is unfortunate the most ideal stress relieving treatment may precipitate an undesirable phase in a given alloy and impair the corrosion resistance. In such instances, the precise merits of the stress relief *vs.* the deleterious effect on the corrosion resistance must be weighed to establish the most logical approach.

Flash butt welding of austenitic stainless steels to themselves and other alloys has been an accomplished fact for many years but size has been somewhat of a limitation because of the upset pressures required. Also, steel technology was not necessarily adaptable to stainless steels. Recent work (*2D*) has shown that heavy sections of stabilized stainless steels can be flash butt welded. Heavy equipment is required to reach the necessary upset pressures, and argon shielding is essential to prevent the formation of a chromium oxide skin and resulting joint deficiencies. Preliminary results show that the stabilized alloys are not susceptible to intergranular corrosion. Another somewhat similar area of interest for the future is friction welding of large sections.

In the past, controversy has revolved around the effects of bright annealing of austenitic stainless steels. Though there is some hydrogen absorption from the bright annealing atmosphere, this has presented no problem for equipment in service. However, the effect of hydrogen can be seen by a decrease in tensile strength and ductility resulting from the formation of martensite during the deformation encountered in tensile testing at very low speeds.

A recently developed alkaline/acid/alkaline passivating treatment requiring 2 hours has eliminated rusting on free machining stainless steels. Formerly, conventional passivating treatments caused some rusting. This was due to trapping of acid in the pits left on the surface as the result of the passivating solution's attack on the nonmetallic inclusions present on the surface.

Users of stainless steel alloys in the chemical industry sometimes have a tendency to overlook the importance of fasteners used in conjunction with their equipment. This, of course, can be disastrous, and a review by Layton and White (*4D*) describes many important aspects of fasteners. In addition to citing the characteristics of the less expensive coated fasteners, the authors also consider in detail the merits of stainless steels and higher alloys as well as fastener technology, design, and corrosion.

LITERATURE CITED

Corrosion

(1A) Aust, K. T., Armijo, J. S., Westbrook, J. H., *Am. Soc. Metals Trans. Quart.* **59**, 544–56 (1966).
(2A) Evans, T. E., Burr, D. J., *Brit. Corrosion J.* **1**, 192–8 (1966).
(3A) Hospadaruk, V., Petrocelli, J. V., *J. Electrochem. Soc.* **113**, 878–83 (1966).
(4A) Luce, W. A., Peacock, J. H., IND. ENG. CHEM. **58**, 57–60 (1966).
(5A) Saxena, M. N., thesis submitted to University of Wisconsin, 1965.

Industrial Applications

(1B) Butler, T. J., Carter, P. R., *Electrochem. Technol.* **3**, 157–61 (1965).
(2B) Herbsleb, G., Schwenk, W., *Werkstoffe Korrosion* **17**, 745–51 (1966).
(3B) International Nickel Co., Bulletin **CEB-4** (1966).

High Temperature

(1C) Puyear, R. B., Silence, W. L., *Mater. Protect.* **5**, 17–19 (1966).
(2C) Simmons, W. F., Van Echo, J. A., ASTM Data Ser., Publ. **DS5-S1** (1965).

Alloy Development—Manufacturing & Fabrication

(1D) Bernstein, A., Carlen, J. C., Rick, L., *Welding J. N.Y.* **44**, 504s–8s (1965).
(2D) Groebler, H., Muller, H., *Mitt. Deut. Forschungsgesellschaft Blechverarbeitung* **17**, 118–30 (April 15, 1966).
(3D) Jones and Laughlin Steel Corp., Brit. Patent **1,029,814**.
(4D) Layton, D. N., White, P. E., *Brit. Corrosion J.* **1**, 213–23 (1966).
(5D) Smolinski, J., *J. Iron Steel Inst.* **204**, 57–8 (1966).