

MATERIALS OF CONSTRUCTION

Iron, Carbon Steel, and Alloy Steel

IN THE three-year period 1956 through 1958 the iron and steel industry has witnessed the development of ferrous products with considerably higher strength and better notch toughness than were previously available. In alloy steels, the push to outer space has spurred the creation of steels with tensile strengths of 250,000 p.s.i. and higher. Quenched and tempered alloy steel with 90,000 p.s.i. minimum yield strength has found extended application in bridges and pressure vessels. The greater strength of tubing, casing, and pipe has been instrumental in expanding their usage because of the economies obtainable. The trend toward improved notch toughness has been evident in carbon as well as alloy steels, and even the cast irons feature improved strength and toughness. Developments in welding rods and welding processes have contributed to the general technological advance, for fabrication processes must keep pace with products to justify and extend their use.

Where corrosion is a factor, testing and research have expanded the applications of iron and steel. Ductile cast

iron, for example, has satisfactory corrosion-resisting qualities and can frequently be used where gray cast iron, malleable iron, or steel is normally used. Resistance of API N-80 steel to sulfide corrosion cracking is improved by a tempering heat treatment at 1100° to 1150° F. In the field of nuclear power, the corrosion rate of carbon steel is sufficiently low to permit the design of a carbon-steel reactor, although more information is needed on the effect of corrosion products. Experimental steels containing nickel, copper, and phosphorus are much more resistant to corrosion than carbon steels in marine applications.

Iron

Wrought Iron. The A. M. Byers Co. (34) has developed a new and improved wrought iron by increasing the deoxidation of the base metal, increasing the relative amount of phosphorus, and using a more siliceous silicate fibrous material. Tests indicate greater uniformity, improved mechanical properties, and superior resistance to many corrosive media.

Cast Iron. Nodular or ductile cast iron, made with magnesium or cerium additions, has sufficient ductility to extend its use widely in many applications (7A). A new process for the production of nodular iron involves cheaper addition agents which do not require other diluting elements that may be undesirable in the final casting (2A). The recommended addition agent is a mixture of sodium and magnesium chlorides with calcium silicide as a reducing agent.

Tests at 800° F. on a series of gray cast irons (5A) indicate that molybdenum is the most potent of the elements studied for improving the elevated temperature properties and that Cr-Mo iron has the best over-all properties. An unalloyed, ferritic nodular iron was far superior in thermal-shock resistance to any gray irons tested.

Ferritic malleable irons have crack-starter drop-weight transition temperatures of -60° to -10° F. (6A), which are as good as or better than those obtained on carbon steels. As with nodular irons, the transition temperature increases proportionally with phosphorus content. With a phosphorus content below 0.03%, the transition temperature is below -150° F. The notch ductility of ferritic malleable iron is insensitive to

section size if there is no primary graphitization.

Pearlitic malleable irons of the reheat-treated and air-quenched and tempered type have drop-weight transition temperatures between 10° and 70° F. for Brinell hardnesses of 160 to 190; with higher hardnesses transition temperatures are higher (6A).

Technical advancements in pearlitic malleable iron are indicated by Joseph (44), who reports the use of bismuth to prevent formation of primary graphite in castings 2 inches or larger in cross section. Bismuth also improves mechanical properties. Small amounts of boron are added to counteract the detrimental effects of chromium. Boron also permits speeding up the annealing cycle appreciably. An oil-quenched and tempered pearlitic malleable iron was developed with a minimum yield strength of 85,000 p.s.i. and a Brinell hardness of 269 to 302, and malleable irons with Brinell hardnesses approaching 400 were being investigated.

Carbon and Low-Alloy Steels

To obtain increased notch toughness in structural carbon-plate steels, the trend has been toward lower carbon and higher manganese contents. The American Bureau of Shipping in 1956 revised its rules to require 0.80 to 1.10% manganese for its Class B semikilled hull steel, instead of 0.60 to 0.90% (8B). ASTM adopted a similar change for its A 131 specification (2B). Steels developed for ship plate are being considered for applications such as oil-storage tanks, where notch toughness is regarded as important.

To obtain increased notch toughness in thick carbon-steel plates of the ASTM A 212 Grade B type of steel made to fine-grain practice (70,000 to 85,000 p.s.i. tensile strength), spray quenching and tempering have been employed instead of normalizing (11B). This practice is permitted in one company specification (36B) to provide tougher steel for nuclear reactors, and is being considered by specification bodies for increasing notch toughness. Gross, Kottcamp, and Stout (11B) studied the influence of quenching and tempering on A 212 Grade B and other carbon and low-alloy steels; such a treatment may be increasingly used on materials with relatively low hardenability to obtain better strength and toughness.

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The Japan Steel Works has introduced a quenched and tempered carbon steel with a minimum yield strength of 65,000 p.s.i., called Welcon-2 H (13B). The composition is cited as 0.18% maximum carbon, 1.35% maximum manganese, and 0.55% maximum silicon. As plate thickness increases, small amounts of alloying elements may be added to maintain the desired properties. The heat treatment gives higher strength and better notch toughness. Because of the lean composition, however, tempered martensite would not be obtained except in light gages.

In the United States, carbon-plate steels have not been as low in carbon or as high in manganese as those developed in Europe (Colvilles' Coltuf 28 steel, Lloyd's XNT steel, British standard N.D. IV steel), but there is a trend in this direction. For example, a semi-killed steel containing 1.00 to 1.35% manganese has been investigated for possible use as a ship-plate material (33B).

To obtain better notch toughness in carbon-plate steel, particularly semi-killed, some European mills have employed low-temperature hot rolling for the last several rolling passes (34B). This produces a finer ferrite grain size and lowers the ductility transition temperature about 30° F. An attendant decrease in the rate of production plus more difficulty in rolling has apparently prevented its adoption in the United States.

Great Lakes Steel Corp. (30B) has reported hot-rolled, niobium-bearing carbon-steel sheets and plates with improved yield strength and notch-toughness characteristics. The higher yield strength that can be developed with niobium is fairly well known, but further data on notch-toughness properties are required, for some unpublished studies have indicated that niobium decreases the notch toughness of hot-rolled steel.

Wiester (37B) in Germany claims that increased strength and notch toughness can be obtained in normalized carbon-plate steel by higher aluminum and nitrogen contents. The aluminum nitride must be of a certain particle size (apparently requiring accelerated cooling from the solution heat-treating temperature down to about 1830° F.) so that a very fine grain size may be obtained upon subsequent normalizing. A small amount of vanadium appears to be necessary to avoid excessive bubbling in the mold due to the higher nitrogen content (15B). This can be an important development if the steel can be readily produced commercially.

Parker (24B) has reported that the yield point of annealed or hot-rolled steel can be increased significantly without any deleterious effect upon notch toughness by straining 5 to 8% and subcritically treating at 900° to 1300° F.

The favorable combination of properties is said to be associated with formation of a substructure.

For nuclear-shielding applications, a low-manganese steel reduces radioactivity hazards and permits more rapid accessibility for repair work (4B, 10B). The composition is about 0.20% carbon, 0.10% manganese, 0.20% silicon, 0.20% titanium, and 0.10% aluminum. Mechanical properties are said to compare favorably with those of the usual carbon-steel grades, and elevated-temperature tensile data indicate freedom from strain aging.

A summary report (39B) on the graphitization of steel in petroleum-refining equipment showed that the carbon-steel grade with the least tendency to graphitize was ASTM A 285. The tendency was greatest in steels containing over 0.015% aluminum, but limited data prevented establishing any relationship between nitrogen content and graphitization. Nitrogen contents of 0.012 to 0.014% seemed to be responsible for inhibiting graphitization in cold-rolled, high-carbon steel strip (29B).

Morgan and Shyne (20B-23B) have described the development of a boron-treated, nonaging rimmed steel in which the boron is added to the mold. Several thousand tons of sheets of this steel have been used in fabrication of automotive panels and in other applications. The commercial practicability of this development may require further evaluation because of variability of the aging tendency and the surface quality of the product, but the development has focused attention on the desirability of nonaging steel with surface quality as good as that of rimmed steel and has advanced the understanding of the strain-aging process in mild steel.

Of major interest to manufacturers of parts that require considerable machining has been the increased use of leaded steels. New technical information confirms that the principal function of lead is reduction of friction between the chip and the cutting tool, resulting in lowered cutting temperatures and a reduced tendency for the chips to adhere to the tool (27B, 28B). Except that the presence of lead appears to lower fatigue strength somewhat at high strength levels, addition of lead to steel does not adversely affect mechanical properties to any marked degree (7B, 35B). In fact, lead refines the grain size in some steels.

La Salle Steel Co. is employing a new method for obtaining high strength and good ductility in bar steel without heat treating (31B). This method, which consists of drawing the bars at elevated temperatures (up to the lower critical), results in greater uniformity of mechanical properties in carbon bar steel than does heat treatment.

In reinforced-concrete construction, sanction by the American Concrete Institute of the use of ultimate-load design procedures has led to higher stresses in reinforcing steel than were previously permitted. For maximum advantage to be realized from the new design procedure, reinforcing bars with yield points higher than those previously available were needed. The highest minimum yield point provided by previous ASTM specification was 50,000 p.s.i. Under a new ASTM specification (3B) reinforcing bars for use in columns can be purchased to a minimum yield point of 75,000 p.s.i.; a specification covering reinforcing bars with a 60,000 p.s.i. minimum yield point for use in flexural members is forthcoming.

In the oil-well industry, the trend has been toward higher strength levels. The American Petroleum Institute adopted a P-105 grade of tubing (1B) with a minimum yield strength of 105,000 p.s.i., compared with a previous minimum yield point level of 80,000 p.s.i. A P-110 grade (1B) was adopted by API for casing with a minimum yield point of 110,000 p.s.i.

A new grade of hot-rolled and expanded line pipe (X-56) was developed with a minimum yield point of 56,000 p.s.i. (26B). The highest yield strength previously available for this type of product was 52,000 p.s.i. Quenched and tempered steels having yield strengths up to 110,000 p.s.i. are being investigated (38B) and should be available in the future.

A wide choice of resin-based coatings for protecting and beautifying steel surface ranges from alkyls and phenolics to cellulose and vinyls. Frequently, such coatings are applied as a final step on a finished article, but a noteworthy innovation is the production of vinyl-coated sheet that can be subsequently formed and drawn without damage to the coating (12B, 14B, 19B). The toughness and decorative value of the colored vinyl coatings should result in numerous applications.

The development of porcelain enamels that fire in the temperature range 1400° to 1450° F., a decrease of approximately 100° F. from the range previously in general use, has provided a means of lowering furnace operating costs and minimizing objectionable distortion of the enameled article. These enamels have been adopted in the appliance trade (17B). They are being promoted for use on rimmed cold-rolled sheets as a further cost-reduction proposal, and the extent to which this program succeeds will have a marked influence on future markets for the higher priced low-metalloid enameling steels. Although the cold-rolled steels,

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because of composition, sag more under their own weight than enameling steels during enamel firing, this difference in behavior becomes less pronounced as firing temperatures are lowered.

Concurrent with the introduction of the 1400° F. two-coat enameling practice has been renewed interest in a one-coat, or direct-white, enameling practice. A comprehensive review of the problems involved in direct-white enameling and past efforts to resolve these problems, recently published by Petzold (25B), describes both American and foreign studies.

Two approaches to the direct-white problem are now under active development in America. The one involves the use of precoated steel sheets specially treated by the steel supplier to render them suitable for one-coat enameling (5B, 6B, 32B). A similar approach has been adopted in England, where Nitec, a product of John Summers and Sons, is reported to be in commercial production (16B). The second method involves a modification of the pretreatment practices used in the enameling plant, particularly the pickling process. Advocates of this technique are optimistic about the possibilities of phosphoric acid pickling, particularly on cold-rolled sheets (9B, 18B).

Alloy Steel

Developments in alloy steels reflect the growing trend toward higher allowable stresses in the design of structures. By judicious selection of the steel to provide an appropriate combination of strength and ductility or toughness, a greater part of the high strength can be utilized in design.

Good examples of the use of the high-strength alloy steels are found in the field of astronautics, a science that has grown in importance since Sputnik I was launched in late 1957. The need for weight saving in the field through the use of lighter, stronger materials is great, for the structural weight of a long-range ballistic missile goes up 30 pounds for every additional pound of useful load (9C). Medium-carbon alloy steels, particularly in sheet form, are being evaluated for use in the motor cases of solid-propellant missiles (corrosive liquid fuels require more corrosion-resistant steels). Sheet materials of steels, such as AISI 4130 and AISI 4135, heat-treated to yield strengths of about 160,000 to 180,000 p.s.i., have been used for some time, but the demand for greater thrusts and longer ranges of travel for missiles created a need for higher strength, and sheets of AISI 4340 and AISI 4335 modified with vanadium have been evaluated for yield strengths of 200,000 p.s.i. and

slightly higher. Even higher strengths are envisioned, and many new alloy steels have only recently been developed and are being evaluated for application at yield strengths of 230,000 p.s.i. and higher (27C). Because most of this work is recent and is classified, very little information is available.

In a related area, two Dutch investigators issued a brief report in 1954 on the development of exceedingly high strengths in alloy steels (13C). The process consists of cooling from the austenitizing temperature to a subcritical temperature at which the austenite is unstable, deforming the metal at this temperature, and then quenching and tempering at a low temperature. Since then, several workers have investigated this process. Schmatz and Zackay (19C) have reported yield strengths in excess of 300,000 p.s.i. and elongations of 6 to 8% on a 0.40% carbon, relatively high-alloy steel, by deforming 75% at 1000° F., followed by quenching and tempering at 500° F. Kula and Dhosi (12C) observed strength increases for AISI 4340 from a similar method of processing, but the impact properties were adversely affected.

In the development of new alloy steels and modification of present ones, extensive use has been made of the fact that silicon provides resistance to softening when martensitic steels are tempered in the range of 500° to 700° F., and raises the so-called 600° F. embrittlement temperature (20C, 22C).

Research has been conducted on the effect of hydrogen on the mechanical properties of heat-treated alloy steels, particularly those heat treated to tensile strengths considerably above 200,000 p.s.i. for aircraft applications. This work has been stimulated by the tendency of these ultra-high-strength steels to be embrittled by the hydrogen picked up during the cleaning and plating processes and has in some measure led to improved techniques for minimizing the deleterious effect of hydrogen (3C, 8C, 11C, 16C).

The 9% nickel steel (ASTM A 353), although not yet used extensively, has been increasingly recognized where good notch toughness at low temperatures (−320° F.) is required in combination with moderately high strength (1C).

The use of heat-treated low-alloy steels of high strength as constructional materials has continued to increase since the satisfactory performance of quenched and tempered steel in pressure vessels was demonstrated (2C). Recognizing the need for increasingly careful design and workmanship for material with 90,000 p.s.i. minimum yield strength, the ASME Boiler Code (14C) issued a revised case covering the use of

a quenched and tempered steel for pressure vessels. An increase in yield strength from 90,000 to 100,000 p.s.i. and in maximum allowable stress from 26,250 to 28,750 p.s.i. has also been permitted (15C). The Pressure Vessel Research Committee of the Welding Research Council has continued its intensive evaluations of the higher strength steels for pressure vessels (6C).

In bridge construction, the use of a quenched and tempered high yield-strength alloy steel (90,000 p.s.i. minimum yield strength) and of a hot-rolled high-strength, low-alloy steel (50,000 p.s.i. minimum yield strength) for critically stressed members resulted in a substantial savings in the cost of the Carquinez Straits Bridge near San Francisco, Calif. (7C).

As a result of the catastrophic brittle service failures (4C, 5C, 18C), of large steam-turbine and generator rotor shafts since 1954, the American heavy-forgings industry has intensified its efforts to develop improved notch toughness in rotor steels. Much has been done by individual manufacturers as well as by industry cooperation through the ASTM Task Group on the Brittle Fracture of Rotor Forgings. Whereas Ni-Mo-V rotors today have V-notch Charpy 50% shear transition temperatures of 70° to 120° F., it was not uncommon several years ago to observe transition temperatures as high as 250° F. New research promises the development of rotor steels with transition temperatures somewhat below room temperature.

For several years, the heavy forgings industry has known that small amounts of hydrogen have an adverse effect on the ductility and the susceptibility to flaking of forging steels. Experimental work by Kerlie and Richards (10C) showed that the water content of the furnace atmosphere, the slag basicity, and the degree of oxidation of the slag-metal system largely control the hydrogen content of the liquid steel during basic open-hearth steelmaking. Even with good control, however, the probable lower limit of hydrogen content appeared to be 2 to 3 p.p.m., not sufficiently low for freedom from flaking in the large forgings. Accordingly, vacuum casting has been adopted in the United States, as in Europe, and, by its use, hydrogen contents of no more than about 1 p.p.m. may now be obtained. Vacuum-cast forgings are immune to flaking. The outstanding success of vacuum casting in the United States is reported by Orehsoski and Hornak (17C).

Mechanical Properties

In many product areas, improved notch toughness has been emphasized to prevent brittle fracture in service.

Several good surveys indicate the factors influencing notch toughness (1D, 4D, 5D, 7D). In unhardened pearlitic steels the best toughness (lowest transition temperature) is obtained with low carbon, phosphorus, and nitrogen contents, with increased manganese, nickel, silicon, and aluminum, and with finer ferrite grain size. For the hardened, heat-treated steels, notch toughness is dependent mainly upon microstructure, but individual elements may have an influence. In general, the lower the temperature of transformation, the better the toughness. To develop superior notch toughness when the transformation temperature is low, tempering is required, but tempering embrittlement must be avoided (10D). Small amounts of high-transformation-temperature product, such as pearlite and upper bainite, may seriously impair the notch toughness of tempered martensitic steels (3D, 4D).

In the evaluation of notch toughness, the V-notch Charpy impact test is the most widely accepted, but its deficiencies have led to the development of other testing techniques. One of the best of these for determining the so-called ductility transition temperature is the crack-starter drop-weight test. Pellini (6D) and Puzak (9D) have adequately covered the advantages of this type of test for evaluating both base metal and weldments of various steels. Puzak, Babecki, and Pellini (8D) have shown the correlation between a number of brittle-fracture service failures and drop-weight and Charpy tests. Recent data indicate that changes in the drop-weight testing technique are required to obtain more appropriate measures of the ductility transition temperature.

The strength of structural steel columns is significantly different from (usually less than) that given by theoretical formulas. Under sponsorship of the Column Research Council of the Engineering Foundation, Lehigh University (2D) has found that for columns made of steel exhibiting yield-point behavior, residual stresses in the columns are instrumental in developing a yield strength appreciably lower than that predicted by theory. The residual stresses arise mainly from cooling from the hot-rolling temperature. The results are expected to provide a sounder basis for designing steel columns.

Welding

Several new welding processes appear to have considerable promise. One is high-frequency resistance welding for the joining of sheets or light-gage plates (4E). With high-frequency current conduction, the welding current can be made to follow a narrow path along the edges to be joined, and high speeds of

welding can be attained, such as 400 feet per minute for seam-welded tubing when a frequency of 450,000 cycles per second is used.

The use of carbon dioxide as a shielding atmosphere in metal-arc welding has been a significant development (2E), for it permits use of a cheaper shielding gas, eliminates slag-removal problems after welding, and provides a high deposition rate. A further development in this field is the addition of oxygen to the CO₂ shielding gas (5E). The oxidizing effect of the CO₂ and O₂ atmosphere is balanced by suitable quantities of deoxidizers in the bare-steel-wire electrode. The exothermic reaction results in deep penetration, and the deposition rate is high because of the very high density of the welding current used. The welds contain very low hydrogen and exhibit low crack sensitivity.

Russian literature has described a novel welding method, electroslog welding, which permits single-pass welding of extremely thick components and does not require edge preparation of plates to be welded (1E). The heat developed is obtained by the passage of current from one or more automatically fed filler wires through a substantial layer of electroconductive molten slag that melts both the filler wire and the adjacent plate edges.

Conventional alloy steels frequently require preheating before welding to ensure a desirable microstructure in the heat-affected base metal. For the low-carbon, quenched and tempered alloy constructional steels preheating is not generally necessary, because the low-carbon martensitic microstructures have adequate toughness and ductility. In fact, preheating can unfavorably affect properties because of the resultant formation of mixed microstructures of ferrite and high-carbon martensite. Using simulated welding thermal cycles, Nippes (3E) studied United States Steel's low-carbon, quenched and tempered "T-1" constructional alloy steel. When preheat or unusually high heat inputs are used in the welding of "T-1" steel, these factors must be controlled within specified limits to obtain adequate toughness in the heat-affected zone of the base metal.

Corrosion

Cast Iron. The corrosion resistance of ductile cast iron has been reviewed by LaQue (20F). Any differences in corrosion behavior among gray cast iron, ferritic and pearlitic ductile cast irons, and mild steel are attributed to differences in the amount of carbon present and the form in which it occurs. Carbon, either as graphite or carbides, is more noble than the iron matrix and

therefore acts as the cathode in local corrosion cells. However, graphite is insoluble in most environments in which cast irons are used, and will be left as a residue on the surface. This layer, intermixed with insoluble corrosion products, may form an impermeable barrier to the further penetration by corrosive liquids. Data for corrosion in acids, in neutral and alkaline solutions, in sea water, in the atmosphere and underground, and under conditions involving erosion, indicated that ductile cast iron has satisfactory corrosion-resisting properties and generally can be used where gray cast iron, malleable iron, or steel is regularly used. Laboratory and service tests indicated that ductile cast iron gives satisfactory service in piping in petroleum tankers (24F).

Cathodic protection has been used in a brewery to prevent corrosion of cast-iron liquor tanks (16F). Previously widespread pitting and rust nodules were observed on the sides and bottoms of tanks after 15 years of service. The use of painting or of magnesium anodes for cathodic protection was ruled out because of the possibility of product contamination. Cathodic protection by impressed current with inert anodes effectively suppressed corrosion and did not cause product contamination.

Steel. Electrical-resistance probes were used by Schaschl and Marsh (27F) to determine the effect of dissolved oxygen on corrosion of steel and on current required for cathodic protection. In laboratory experiments of several days' duration, they found that the corrosion rate of steel in neutral aqueous solutions is determined by the dissolved oxygen available at the surface of the steel. Any factor affecting diffusion of oxygen has a marked effect on corrosion rate. The minimum current density needed for cathodic protection is about 20% greater than the local-cell current associated with corrosion. Therefore, by measuring the corrosion rate of an unprotected specimen, it should be possible to compute the minimum current density needed for cathodic protection in the field. The electrical-resistance method allows direct observation of corrosion rate while corrosion is in progress and can be used in plant corrosion studies. However, the corrosion rate of a probe is not always the same as that of a large structure in the same environment.

Some aspects of the stress corrosion cracking of steel in caustic soda solutions have been discussed by Champion (6F). Plant experience with the Bayer extraction process indicates that the most important factors in this type of cracking are tensile stress, sodium hydroxide concentration, and temperature; a rise of any of these accelerates stress corrosion.

Serious cracking can probably be avoided by keeping the uncombined soda concentration below 200 to 250 grams per liter of sodium oxide or keeping the temperature below 192° F. The most effective precaution is to stress-relieve mild-steel equipment after fabrication and assembly. However, careful fabrication and assembly can reduce residual stresses in riveted and welded structures.

Parkins (25*F*) attributed stress corrosion cracking of mild steels in nitrate solutions to an increase in energy along grain boundaries caused by carbide particles, plastic deformation, and application of stress. The energy of the grain boundary regions is sufficiently above that of the grain centers for corrosion to remain concentrated along the less noble boundaries. Formation of an acid solution of ferric nitrate as an anodic product at the tip of the cracks prevents stifling of the corrosion reaction. Advancement of stress corrosion cracks by the simultaneous action of corrosion and mechanical tearing is postulated.

Dawson (7*F*) reported that anhydrous ammonia, as stored and distributed for agricultural uses, can produce stress corrosion of steel. A survey has indicated that 3% of the pressure vessels in agricultural ammonia service failed within 3 years. Stress corrosion of steel is attributed to an unknown impurity in the agricultural ammonia, because steel pressure vessels have given many years of satisfactory service in other ammonia applications. Vessels subject to failure were manufactured with cold-formed heads and had not been stress-relieved after fabrication. For agricultural ammonia service, pressure vessels should be stress-relieved after fabrication to reduce high residual stresses and minimize the possibility of stress corrosion in service.

Stress corrosion cracking of steel by hydrogen sulfide environments continues to be the subject of extensive research. Vollmer (32*F*) has summarized the significant developments and lists measures for minimizing cracking in high-pressure, sour-condensate wells. Cracking of steel in sulfide environments may be the result of true stress corrosion, hydrogen embrittlement, or a combination of these two mechanisms. The sensitivity of steel to stress corrosion is related to hardness and may be associated with the presence of martensite and some of the microstructures obtained by tempering martensite. Chemical composition of steel influences sensitivity to sulfide cracking only in so far as composition determines hardenability. Plastic deformation, as in cold straightening of tubing, increases the sensitivity of susceptible steels. Tempering of API N-80 tubing, at not less than 1150° F. after the usual normalizing treatment, is

proposed for minimizing cracking caused by sulfide environments. To provide a margin of safety, the yield strength of N-80 steel for sulfide service should be limited to 90,000 p.s.i. maximum. Efforts should be made to minimize stresses in all equipment and avoid deep tong marks and other mechanical gouges.

The results of an extensive research program on hydrogen sulfide stress corrosion cracking of steel have been presented by Schuetz and Robertson (28*F*). These authors concluded that the basic cause of failure in sulfide environments is associated with the absorption of hydrogen and that the principal factors determining failure in service are internal stress, the magnitude of applied stress, and hydrogen content. Martensitic and ferritic structures are susceptible to failure when the stress level and hydrogen content are sufficiently high; however, failures were not produced in austenitic structures.

The development of a steel with the mechanical properties of API N-80 but a better sulfide stress corrosion resistance has been described by Cauchois, Didier, and Herzog (5*F*). The new steel, APS 10 M4, is a chromium-aluminum-molybdenum alloy heat-treated to obtain a structure of "carbon-free" ferrite with highly dispersed fine carbides. A number of laboratory tests indicated that the new steel is more resistant to hydrogen sulfide than other steels, including API N-80 steel. After 6 months of testing, it was determined that the steel is sufficiently resistant to hydrogen sulfide to be satisfactory for use at the Lacq gas field in France.

Laboratory and field methods for quantitative study of sulfide corrosion cracking have been described by Fraser, Eldredge, and Treseder (12*F*). Statistical techniques were used to develop a number called the critical strain, at which the probability of failure under the specific test conditions is one half. In a study of 104 steel compositions (11*F*), it was possible to derive predictive equations for rating the cracking susceptibility of a new steel from its composition, mechanical properties, and heat treatment. Resistance to cracking is increased by increases in ductility and in carbon content, and decreased by increases in hardness, strength, and manganese and molybdenum content. The resistance to cracking of N-80 steel can be markedly improved by tempering for 1/2 hour at 1100° F.

The susceptibility of AISI 4140 steel bolts to sulfide corrosion cracking increases with increasing bolt hardness, applied stress, and amounts of plastic deformation, and decreasing test temperature (34*F*). An electroplated coating of nickel on bolts protected against

cracking, but electroplated coatings of cadmium, zinc, lead, and chromium did not give reliable or consistent protection. Corrosion inhibitors reduced but did not eliminate cracking.

Larrabee (21*F*) has reported that experimental steels containing nickel, copper, and phosphorus are much more corrosion resistant in marine applications than carbon steels customarily used as sheet piling. The superiority of the Ni-Cu-P steels was evident in and above high tide in sea-water piling tests and in atmospheric exposure tests 80 feet from shore. In the latter tests, the most resistant Ni-Cu-P steel had a weight loss only 5% that of carbon steel.

Information on the underground corrosion of ferrous metals, including wrought iron, cast iron, steel, stainless steel, and coated products, reported by the National Bureau of Standards (26*F*), includes the results of tests at 128 locations in the United States and laboratory studies on the electrical and electrochemical aspects of underground corrosion. All ferrous materials with relatively low alloy content showed similar corrosion patterns in a given soil environment, although the type and amount of corrosion varied widely in different soils. The use of galvanized and bituminous coatings on pipes and cathodic protection are discussed.

Atmospheric corrosion data on 10 structural steels in tropical environments were reported by Southwell, Forgeson, and Alexander (30*F*). The tropical marine atmosphere of the Canal Zone was 1.5 to 2.2 times more corrosive to steel than temperate marine atmosphere. Copper in steel was not as effective in retarding corrosion in tropical atmospheres as in temperate zones. Nickel and chromium steels were very effective in resisting corrosion in the tropical exposures. Four proprietary high strength, low-alloy steels displayed good resistance to tropical atmospheric corrosion.

The effect of alternate corrosion and abrasion on 11 ferrous metals was investigated by Dearden and Swindale (8*F*). Panels were exposed in an industrial atmosphere until a control panel had achieved a standard increase in weight, and then were subjected to controlled abrading with emery cloth. This procedure was repeated for several cycles. In general, resistance to corrosion was reduced by abrasion, and increasing frequency of abrasion increased the corrosion rate. Three white cast irons showed exceptional resistance to corrosion, even when combined with abrasion. The slow-rusting qualities of a high-strength, low-alloy steel were not developed under frequent abrasion.

Larrabee and Mathay (22*F*) reviewed the types of constructional materials resistant to the many corrosive environ-

ments in coal-chemical plants. The protection of structural-steel work by paints was viewed from the standpoint of minimizing maintenance costs. To reduce the corrosive attack, copper steels and high-strength, low-alloy steels are frequently used for outside structural-steel work. Stainless steels were satisfactory for most process applications.

Carbon steel was attacked in corrosion tests conducted by Vreeland and Kalin (33F). In the nitrogen fertilizer solutions, aluminum and several chromium and chromium-nickel stainless steels were not attacked. In the complete-mix fertilizer solutions, only the chromium-nickel stainless steels were not attacked. The 12% chromium stainless steels similar to AISI Type 405, the chromium-nickel stainless steels, and aluminum should be suitable as constructional materials for tanks for nitrogen liquid fertilizers and the chromium-nickel stainless steels should be suitable for complete-mix fertilizers.

Hackerman, Hurd and Snively (14F) reported results of corrosion studies conducted with mild steel in solutions of ammonium nitrate, ammonia, and water at 30°, 45°, and 60° C. The corrosion reaction was markedly affected by stresses in the metal, to the extent that completely stress-relieved coupons would not corrode. The corrosion rate was much lower at 45° and 60° C. than at 30° C., an indication of a change in the corrosion mechanism at the higher temperatures. The effects of sulfur- and arsenic-containing inhibitors were also studied. When ammonium thiocyanate in concentrations greater than 0.1% was added at 30° C., the corrosion rate dropped from 370 to approximately 25 mg. per sq. dm. per day. At 45° C., inhibition was most effective with a combination of 0.05% 2-mercaptoethanol and 0.05% sodium arsenite, followed closely by a combination of 0.1% ammonium thiocyanate and 0.05% sodium arsenite. Thiocyanate and thiourea alone at concentrations of 0.1% were less effective.

Carbon or low-alloy steel as a material of construction for atomic power plants in place of stainless steels would reduce the cost of atomic power. Blaser and Owens (2F) have investigated the corrosion of steel in water at 600° F. The corrosion rate was highest at the start of a test but decreased rapidly with time of exposure; after 6 months it was approximately 0.0001 inch per year. Sufficient information is available to permit the design of a carbon-steel reactor, although further work should be done on the amount and effect of carbon-steel corrosion products in reactor systems.

A hydrogen-effusion method of studying corrosion of ferrous metals in high-

temperature water was reported by Bloom and others (3F, 4F). The hydrogen formed by corrosion inside a small sealed container is measured in a vacuum system as it permeates the walls of the container. The corrosion rates corresponded with those obtained by weight-loss methods. An increase in pH to 10.6 with sodium or ammonium hydroxide did not produce a significant change in the corrosion of steel after 200 days of testing at 600° F. Douglas and Zydes (9F, 10F) found no evidence of pitting or other localized attack on iron exposed to high-temperature water at 460° to 680° F. Virtually the same corrosion behavior was observed in saturated vapor and superheated vapor as in the liquid phase. Large increases in pH and dissolved salt content had little effect on the corrosion rate. Corrosion of iron by high-temperature water proceeds by diffusion of iron ions outward from the metal to the oxide-water interface.

Horsley and Maskrey (15F) have studied the effect of adding 250 to 500 p.p.m. of zirconium to liquid bismuth in thermal convection loops at temperatures up to 1150° F. Zirconium nitride formed on the steel surface and reduced the corrosion rate from 0.65 to about 0.17 inch per year. However, the fact that the film occasionally spalled off and was not re-formed allowed corrosion of the underlying steel to proceed rapidly. The zirconium nitride film re-formed if the steel was heavily nitrated, and a lower corrosion rate, 0.010 inch per year, was obtained.

Coated Products. One of the more recent developments in metallic-coated steel is steel strip coating with aluminum by a hot-dip process. This has been used extensively where resistance to oxidation is desirable. Large amounts of aluminum-coated steel are being used in automobile mufflers. It is being investigated on a large scale for applications where resistance to atmospheric corrosion is necessary, such as fencing and wire products (13F) and roofing and siding.

Cast iron was more resistant to heat and corrosion when coated with aluminum by a new hot-dipping process (31F). Application of the coating was followed by heat treatment at 1700° F. to produce a coating composed entirely of iron-aluminum alloy. The coating protects cast iron from scaling in sulfuric and other environments at temperatures up to 1400° F.

Good correlation is reported between rate-of-pickling and iron-solution tests and the corrosion performance of tinplate containers (35F). The studies indicate that the lag time observed in the rate-of-pickling test can be eliminated by annealing the steel in dry hydrogen. Koehler

(18F) reported that stannous chloride inhibits the corrosion of steel in air-free citric acid solution and shifts the corrosion potential in the noble direction. In air-free citric acid containing dissolved tin, coupling of steel to tin reduced the corrosion rate of the steel and the amount of hydrogen evolved. This behavior is not consistent with theory, because an increase in the amount of hydrogen evolved would be expected. The shelf life of a tin can containing a fruit product such as prune juice is visualized as consisting of three periods: a first period in which the tin coating corrodes by reaction with depolarizers; a second in which both tin and steel are exposed and the corrosion processes are those of the tin-steel couple; and a third in which the can is detinned and the steel base is attacked (19F). The shelf life is largely determined by the processes occurring in the first two periods. Tin-plate producers and can manufacturers alike are continuing to investigate new methods for evaluating the corrosion resistance of tin plate as an aid to improving the shelf life of containers. Chemically and electrochemically treated black plate has been developed for container application (17F, 23F).

After estimates showed that hot-dip galvanizing would cost either the same as or less than painting, the Celanese Corp. used galvanized structural steel for its new polyethylene plant on the Gulf Coast (29F). All but 5% of the structural works was designed to be single-dipped in 30-foot baths, and was assembled with galvanized bolts and nuts wherever possible.

Bigos (1F) states that correct surface preparation is the most important requirement for satisfactory painting of steel. The optimum surface preparation consists of complete descaling by blast cleaning or pickling and a suitable pretreatment. For mild atmospheres, wire brushing is adequate and economical; intact mill scale under such conditions is a good base for paint.

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