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THE UNIVERSITY OF ALBERTA

EFFECT OF COLD WORK AND STRESS RELIEF ON SULPHIDE STRESS CRACKING OF HIGH STRENGTH CASING STEEL

by

KATHERINE ANNE McKENZIE

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH IN
PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF
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IN
METALLURGICAL ENGINEERING

DEPARTMENT OF MINING, METALLURGICAL AND
PETROLEUM ENGINEERING

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Abstract

One of the most significant technical problems facing the petroleum industry is alloy cracking in hydrogen sulphide (H_2S) environments. Many questions concerning sulphide stress cracking (SSC) remain unanswered and practical solutions are sought to reduce or eliminate the occurrence of SSC failures.

[illegible] strength steel subjected to cold deformation is known to be susceptible to SSC. Even highly resistant tubulars can fail if improperly handled. There is considerable scope to improve the knowledge of cold w[illegible] failures in sour petroleum production. This project is an initial step tow[illegible] goal.

The SSC resistance of a high strength tubular steel has been tested in the laboratory as a function of cold working and stress relief heat treatment. The standard NACE (National Association of Corrosion Engineers) constant load tension test was used with the H_2S saturated acidic salt water solution. All samples were loaded in tension to 90% of the steel's actual yield strength. Slow strain rate technique (SSRT) testing was also conducted with the same H_2S saturated salt water solution.

Steel specimens became more prone to failure during constant load testing when they had been subjected to increasing amounts of cold work. Constant load tension testing revealed that the high strength steel can develop SSC susceptibility when it is cold worked to 5% strain or above, accomplished by tensile elongation at increments of 0, 5 and 9% permanent strain. (This form of deformation produces homogenous strain in the steel specimen.) However, when the steel was stress relieved prior to cold working, SSC failure did not occur. SSRT tests did not reveal conclusive differences in SSC susceptibility of samples exposed to the same NACE sour solution, but an unequivocal decrease in time-to-failure occurred upon changing test environments from air to the NACE solution.

Examination of failed tensile samples by optical and scanning electron microscopy revealed that the fracture mode becomes more brittle with increasing amounts of cold work.

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1.0 INTRODUCTION

Petroleum production is complicated by the presence of hydrogen sulphide. Sour well blowouts resulting from tubular failures present serious hazards to both workers and the environment. The costs of capping, lost product and lost production can also mount quickly. Assurance of tubular string integrity, therefore, has both social and economic consequences. Further, industrial benefits will accrue to manufacturers who have the technology to produce sulphide stress cracking (SSC) resistant steel.

Recent trends to exploit sour petroleum reserves have intensified the importance of improved SSC resistance. The use of very high strength steels has been prohibited due to SSC susceptibility. Despite tremendous advances in the quality of steel tubulars, failures still occur as increasingly higher strength materials are required for the growing trend toward deep, high pressure sour wells, toward heavy oil with thermal recovery, and as older petroleum fields become slightly sour. In order to develop better steels, and to be able to select the best grade for specific circumstances, it is important to understand the mechanisms of SSC and their interaction with cold work. It is difficult to prevent sulphide cracking simply by the addition of chemical inhibitors. Therefore, the selection of resistant materials is important to prevent abrupt and often catastrophic SSC failure.

The main requirements for production of tubulars resistant to SSC are low sulphur levels (clean steel), sulphide shape control, and high temperature tempering combined with optimum chemical composition in order to obtain a uniformly tempered martensite microstructure.[8,19,21,43,46,49] Despite great improvements in steel composition and processing, the highest usable strength of tubulars in hydrogen sulphide remains around 690 MPa (100 ksi).[12,19,23,49,52]

A stress relief, double tempering heat treatment may further improve SSC resistance.[16,21,25,51] A 110 ksi-grade material has recently been developed with the NACE threshold stress set at a minimum of 80% of its specified minimum yield strength.[31] The good SSC resistance was attributed to a fully quenched martensitic microstructure, a high tempering temperature, spherical and uniformly dispersed carbides, optimum concentrations of Cr, Mo, V and Ti, and fine grain size. It is also worth noting the very low sulphur content of 0.003%. SSC has been avoided to some extent by use of restricted yield strength steel with a Rockwell hardness below 22 HRC.[12,21,23] However, poor SSC resistance after cold work can occur even if the hardness is below 22 HRC, as it is the microstructure of the steel that is important in preventing SSC.[12,32,52]

SSC tubular failures occur predominantly in or near the coupling, where the material is cold worked by threading and typical make-up procedures.[9,11,22,48] Hoop stresses in standard API connections often exceed 275 MPa (40 ksi), and can approach a steel's yield strength due to make-up alone. Leakage of produced fluids can often occur at connection collars as a result of inefficient sealing, especially at elevated pressures.[9,12,47] Cold straightening may also contribute to SSC susceptibility alone or in combination with other forms of plastic deformation.[2,18,21,49,55]

Factors that can promote failure, such as high stress levels, environmental severity and localized regions of high hardness are not considered in either the current sour service guidelines or the literature.[9,12, 7] An environment can be considered severe for numerous reasons, including particulary low pH (which could result from well acidizing fluids), or an extremely high H_2S content. In addition, benign operating conditions that turn suddenly harsh can contribute to sulphide failure, such as a drop in temperature into the range where the steel is most prone to SSC. It is difficult to control stress and plastic deformation because of the complexity of applying loads during handling and operation of oil field tubulars. Leakage from the formation into the casing tubing annulus for instance, can create conditions of excessive pressure which may contribute to string weight stresses.[9]

Cold deformation is associated with string connections which are by far the most common location for SSC failures downhole. Because of the importance of joints to string integrity, the effect of cold work on SSC resistance is of foremost importance. This project is one step toward solving the problem of SSC of tubular goods.

1.1 Literature Review

Although few in-depth studies on the effect of cold work have been reported, many other important parameters of SSC are well documented. A brief summary of some of the pertinent SSC research is outlined below. The information presented here has been limited to some of the factors which influence the effects of stress relief and of cold work on SSC in high strength steels.

The microstructure most resistant to SSC is a fully tempered martensitic steel.[8,21,31,43,46,49] Tempered martensite is characterised by relatively high toughness for a given strength level. Untempered martensite is a relatively hard, brittle microstructure which is prone to hydrogen embrittlement. However, the properties of martensite are greatly improved by tempering. Metallurgical heat treatment processes leading to the final tempered martensite product are outlined below.

To begin with, the steel is heated into the austenitizing region, (approximately 870°C (1600° F) for an L-80 grade tubular), which causes the steel to assume an austenitic microstructure. Relatively low austenitizing temperatures produce fine-grained austenite which reduces hardenability as compared with coarse-grained austenite. This helps to minimize distortion and cracking during subsequent quenching.[30,31,46] Finer austenite grain size also leads to a tougher, more uniform microstructure.[19,22,30,46] Martensite derived from a fine-grained austenite will also possess a fine structure. This improves toughness since grain boundaries are strong barriers to microcrack propagation.[13] Consequently, grain size has a strong influence on brittle fracture behaviour.

Austenite is rapidly cooled by water quenching to form martensite. Martensite formation causes a volume expansion of several percent.[7,40] Microstructural changes during cooling arise from the fact that the face-centred cubic (fcc) austenitic structure can hold more carbon in solution than the body-centred cubic (bcc) ferritic structure. The carbon atoms trapped in the matrix distort the equilibrium bcc structure which would normally form on cooling, resulting in a body-centred tetragonal (bct) crystal known as martensite.[44] The overabundance of carbon atoms trapped by quenching in a crystal structure that wants to be bcc is what makes martensite hard.[7] Local stresses can be developed in a steel tubular when one section experiences volume change before the adjacent section.[30,40] For instance, the surface of a tubular will transform and expand before the interior steel. These residual stresses can contribute to cracking.[7,30,40]

Tempering is known to improve toughness. This is the result of reducing the distortion of the martensite structure by cardbide precipitation and by movement of dislocations and defects.[7,21,30,51] At sufficiently high temperatures, diffusion of carbon from the strained martensite lattice also helps reduce brittleness. Carbon atoms are then free to coalesce and form discrete iron carbides. There is a trade-off between loss of strength and reducing residual stress for an optimum tempering temperature at a constant tempering time when attempting to maximize the SSC resistance.[12,23,49] With increasing tempering temperature, toughness and the minimum stress intensity for crack propagation (K_{ISSC}) increase, with a reduction in tempering time being necessary to maintain the steel's strength.[7,8,31] It is thought that the strain-free or more-recovered microstructure approaches the most SSC resistant metal.[12,20,46] Crystal imperfections, specifically dislocations, are minimized.[45,51] A minimum tempering temperature of 566°C (1050°F) is specified for API grade L-80. Cold working after the final tempering is forbidden for this class of steel. (An exception to this is API grade C-95 pipe, which is allowed up to 3% compressive cold working after tempering).

The steel's mechanical properties are remarkably affected by the amount of non-metallic inclusions, their shape and distribution.[8,36,43,49,53] If the inclusions are elongated, the ductility and cracking resistance of the steel will be anisotropic. These properties will be much greater when the steel is tested parallel, rather than perpendicular, to the length of the elongated inclusions. The morphology of second phase particles such as manganese sulphide (MnS) and various oxides has a great influence on susceptibility since hydrogen may collect at their interfaces within the steel. Reducing the sulphur content leads to finer, rounder, more homogeneously distributed particles.[2,21,31,43,49] If the surface area of inclusions is also decreased by spheroidizing elongated inclusions, the hydrogen trap density is decreased, hydrogen diffusion is increased and K_{ISSC} increases.[8,53,59] The steel must have good ductility so that cracks do not propagate, because small cold worked spots cannot be prevented in actual service. Crack initiation and propagation are associated with decohesion and/or microvoid formation at the matrix interfaces between carbides and inclusions.[8,43] Thus, homogeneously distributed, small round particles are preferred over the elongated "stringer" inclusions to prevent crack initiation and propagation.[11,49,53] Shape control of sulphide inclusions is accomplished by additions of rare earth metals (cerium or lanthanum), calcium, or zirconium.[20,36] Reducing the number of inclusions by lowering the sulphur content is a more effective way to improve SSC resistance than by spheroidizing elongated inclusions.[11,31,48,53]

Uniform, spheroidized carbides, randomly distributed, are produced with high tempering temperatures, and increase the threshold or minimum stress required to cause SSC failure.[8,20,43,49,51] Needle-shaped carbides which can precipitate at prior austenite grain boundaries, are detrimental to SSC resistance, as they have a notch effect on crack initiation and provide an easy crack path along the weakened boundaries.[20,43]

In conjunction with low sulphur content or "clean" steel, the above metallurgical factors are now recognized as necessary for good SSC resistance.

Steel fabrication methods also affect SSC performance of tubulars. Continuous casting produces less segregation of impurities in steel as compared with ingot production.[46] Water quenching produces less segregation of impurities at grain boundaries than does air cooling, giving quenched steel a higher K_{ISSC}. To achieve through-thickness quenching of thick wall pipe, internal - external quench methods have been developed.[3,12,47,49] Alloying with boron after titanium, aluminum, zirconium.or vanadium have been added to tie up the nitrogen and oxygen in the steel, is also used to attain through-wall hardening.[3,12,30] Inadequate quenching can leave retained austenite which can transform to untempered martensite on cooling after the steel is tempered. Austenite formed when the steel is tempered at too high a temperature also results in untempered martensite. Untempered martensite is a high-stress microstructure and is extremely susceptible to cracking. Tempering after cold deformation decreases the probability of failure in H_2S by relieving residual stresses.[7,12,49] The microstructure most resistant to SSC is a fully tempered martensitic steel.[8,19,21,31,43,46,49]

Double tempering stress relief is used to relieve the quenching and straightening stresses, eliminate retained austenite, and improve yield and impact strengths while maintaining hardness.[21,25,51] Double tempering raises the K_{ISSC} significantly.[16] Retained austenite, which is transformed to martensite on cooling from the first tempering, must be retempered to toughen the newly formed martensite. The second tempering treatment takes place at 10 to 30°C below the first tempering temperature to avoid reducing the hardness.[51] The mechanism of stress relief is thermally-induced dislocation and defect movement, as well as further precipitation and coalescence of carbides.[7,21,23] Thermal energy is required to move dislocations through the crystal lattice. Additional energy is also required to overcome barriers which pin the dislocations, such as solid solution atoms, (mainly interstitial carbon in this structure), stress fields around coherent particles, and dislocation intersections.[13,40] These crystal imperfections reduce the stress around a dislocation so that additional energy must be present to move the dislocation away from the imperfections.[57] Dislocations densities are thus minimized by stress relief heat treatment.[46,51] Recrystallization may take place which reduces internal strains substantially.[30,39,51] Stress relaxation of this nature occurs rapidly during the first hour.[51] Rapid cooling after tempering to avoid temper embrittlement has produced more SSC resistant steel, as documented in past research.[46]

API modified N-80 steel was approved for sour service in 1971. It was incorporated into API Specification 5AC as minimum yield strength Grade L-80. The maximum strength is limited to 655 MPa (95 ksi) and hardness must be below

23 HRC. NACE places a stricter hardness limitation of 22 HRC on this grade, which has been justified and adopted by most steel producers. L-80 tubulars are often stress relieved but this heat treatment is not a requirement as is the case with C-90 grade, which is always double tempered.

1.2 Sulphide Stress Cracking

SSC has been recognized as a problem by the petroleum industry for about 35 years. It has been demonstrated by both lab and field data that H_2S concentrations of only a few parts per million (ppm) can lead to SSC failures.[33,48,57] As well, it is quite rare that water is not present in at least sufficient quantities to cause corrosion.[12,19,47] SSC is a more abrupt and catastrophic form of failure than pitting or severe general corrosion Brittle fracture resulting from the combined action of tensile stresses and corrosion in water and H_2S, is known as SSC.

Sulphide stress cracking is a special case of hydrogen embrittlement. The rate of corrosion is increased in the presence of H_2S by enhancing the anodic dissolution rate.[4,8,12,34] The iron dissolution reaction produces electrons which are consumed by the cathodic reaction. In a low pH aqueous environment containing H_2S, hydrogen is formed by the following reaction:

$$Fe + H_2S \xrightarrow{H2O} FeS + 2H^+ + 2e^-$$

Atomic hydrogen adsorbed on the metal surface (H_{ads}), can combine with other adsorbed hydrogen to form gas or it can diffuse into the steel (H_{abs}). Hydrogen gas harmlessly bubbles away from the metal surface.

$$2H^+ + 2e^- \text{----->} 2\,H_{ads} \begin{array}{l} \text{----->} H_2(g) \\ \text{----->} H_{abs} \end{array}$$

The hydrogen combination reaction is impaired or "poisoned" by H_2S, so that not only are more hydrogen atoms produced by the corrosion reaction, but more atomic hydrogen enters the metal rather than recombining. There have been several theories put forth to explain this poisoning effect. The preferential adsorption of S ions on surface active sites may prevent or slow the recombination of hydrogen. The activation energy to go from molecular to atomic hydrogen, chemisorbed on the metal surface, is thought to be reduced by the presence of H_2S, and the binding energy of dissociated hydrogen may be increased. Even small changes in surface reactions could greatly affect hydrogen embrittlement, since only scant amounts of absorbed hydrogen alter embrittlement behaviour. Once in the metal, atomic hydrogen diffuses or is transported to regions of high triaxial stress, such as grain boundaries, inclusion-matrix interfaces, and crack tips. Trapped at these sites, hydrogen drastically reduces the ductility of the metal.[8,43,49,53]

Crystal imperfections, or defects, are important during plastic deformation.[13,57] When few in number, they cause the metal to be substantially more ductile. The most important defect is a dislocation, which is the region of the lattice separating the distorted and undistorted part of the crystal. When stresses in an area of the metal reach the yield stress, dislocations begin to move, thus providing the mechanism for plastic flow. Dislocations move along preferred paths called slip bands within the crystal structure. A metal which has numerous slip systems will tend to be ductile.[57] A finer grain size provides more grain boundary sites to hinder dislocation movement, but also provides more numerous slip systems which generally means the metal will be more ductile.[13] Fine, spherical carbide particles dispersed in a quenched and tempered steel improve its ductility by providing shorter and more numerous slip bands.[13]

Plastic deformation in crystalline solids is a shearing process that occurs as a result of dislocation movement, and is confined to slip bands within the grains.[7,13,57] Since this deformation is heterogeneous and localized, microcracks can form. Dislocations are able to move through the grain until a grain boundary, inclusion, or other discontinuity is encountered. The dislocations then pile up and create localized stresses. These stresses are relieved or dissipated either by yielding and further plastic deformation, or by nucleation of microcracks at the inclusion-matrix interfaces or at grain boundaries. Two or more microcracks may coalesce to form a macrocrack that can then propagate rapidly.[21,41]

When an external load is applied or when residual stresses are left from quenching or cold working, the driving force for microcracking is increased, or "stress-induced." Cold work increases the strength and hardness of a metal by raising the dislocation density and rearranging dislocations into tangles and eventually cell walls (or deformation cells).[44] Dislocations are produced in numbers proportional to the degree of cold work.[48] Stress relief heat treatments reduce brittleness by dislocation movement and stress relaxation.[7,48]

Embrittlement of steel occurs in regions with the maximum plastic deformation and concentration of stresses, particularly at inclusion-matrix interfaces and at the tips of cracks.[8,20,44,46] Hydrogen embrittlement cracks are known to initiate in regions of high triaxial stress.[21] Sharp, elongated inclusions create a high triaxial stress condition similar to a notch in the steel.[51] Pitting may also create this notch effect.[21,29,55]

With cold work, greater hydrogen solubility is observed.[20,21,23,44,51] Dislocations and internal stresses greatly enhance the solubility of hydrogen in the metal.[21,23,44] Hydrogen can become trapped in the strained zones of dislocations because of this increased solubility. This is thought to impair dislocation movement. The ductility of the steel is then reduced, since yielding and further deformation are impaired. It has been suggested that hydrogen can also reduce bonding forces between iron atoms in the lattice.[20]

Hydrogen embrittlement failures are generally considered to be explained by a combination of the accepted theories.[20] Hydrogen atoms can recombine once they have accumulated at collectors in the metal.[57] This generates very high internal pressures which can contribute to applied or internal stresses, and lead to failure. Hydrogen can also be adsorbed on new crack surfaces thereby reducing the energy necessary for crack initiation and propagation.[20] Other proposed mechanisms are based on atomic hydrogen dissolved in the crystal structure interfering with dislocation movement and slip.[17,29] It has been sugested that hydrogen atoms diffuse into the strained zones of dislocations and become trapped, thus hindering the movement of dislocations.[20] When a sufficient concentration is reached the movement is blocked, creating prime conditions for microcrack nucleation. Troiano and co-workers were able to show that crack propagation is intermittent, and the rate is controlled by the diffusion of hydrogen ahead of the crack tip.[13,41] A minimum hydrogen concentration must be attained before new cracks can form. Environmentally activated cracking of martensite is due to the formation of microcracks as well as the interaction of hydrogen with the advancing crack.[8,17,43]

Hydrogen can also aid in ductile fracture. By collecting at particle-matrix interfaces, hydrogen reduces the cohesive strength of the interface and initiates a void. This may result in the formation of voids at lower strains.[6] Crack growth during ductile fracture involves considerable plastic deformation and energy absorption. Voids grow and coalesce as the bridges of material between them elongate and narrow. As C. D. Beachem found, the ductile fracture surface consists of numerous holes or "dimples" separated by thin walls of material.[13]

All processes leading to homogeneity of the metal in structure, internal stresses, or inclusions, have a positive effect on resistance to hydrogen embrittlement.[8,20,43,49,53] Cracking is affected by environmental factors including acidity and temperature, and by stress and loading parameters.

Higher strength steels are generally more susceptible to SSC and tolerate lower H_2S concentrations before cracking. Similarly, as the applied stress increases, the susceptibility to SSC increases.[12,20] However, a steel's SSC resistance is not uniquely related to yield strength or hardness, but is strongly dependent on alloy microstructure.

Depending on the strength level of the steel, SSC is observed with an H_2S partial pressure greater than 0.003 atmosphere.[49] The occurrence of SSC in high strength steels increases drastically in the range of concentrations from less than 49 ppm (0.005%) to 1% H_2S.[26]

Low alloy steels are more susceptible to SSC with decreasing pH of the aqueous environment between pH 10 and pH 0.[20,21,26] Even over the acidic range of pH 5 to 2, the SSC threshold stress decreases substantially.

The temperature dependence of SSC and hydrogen embrittlement gives a minimum time-to-failure at about room temperature.[12,22,26,57] Susceptibility of high strength steels decreases with increasing temperatures up to 150°C (300°F).[20,26] This can be attributed to hydrogen mobility increasing with temperature.[20] (Also, at 150° C or above, high strength steels such as L-80 can be considered equivalent to lower strength, sour service grades.) Hydrogen diffusion is accelerated by heat, aiding escape from the metal, as well as allowing hydrogen to move along with defects during deformation. This latter effect indicates that dislocations will not be pinned by hydrogen at high temperatures [20] When steel is continuously exposed to elevated temperatures, SSC failure is no longer expected.

API Grade L-80 was developed for sour service and is commonly used in Alberta. This steel is highly resistant to SSC, and both tubing and casing are available in L-80 grade steel.

1.3 Cold Work

Cold work is the plastic deformation of metal at a temperature below its recrystallization temperature. Residual stresses are increased by plastic deformation and it is difficult to predict the magnitude and direction of these internal stresses.[12,21,53] SSC can result from strains arising from the additive effects of operating loads, pressure fluctuations, thermal stresses, and residual stresses during normal operation, start-up or shut-down. Service failures have been observed in a variety of applications where nominal stresses were well below the yield strength of the metal.[35] Stresses are maximized when tubulars are designed with minimum wall thickness because of downhole clearance considerations.[3,12,35] This pertains to both axial and burst loading.

With an older grade N-80 steel in H_2S, 1% permanent deformation reduces the load carrying capacity as much 35%.[2] However, a temper treatment subsequent to cold working renewed its SSC load carrying capacity. Bending a steel below about 500°C can increase the residual stresses up to the yield strength of the metal.[21]

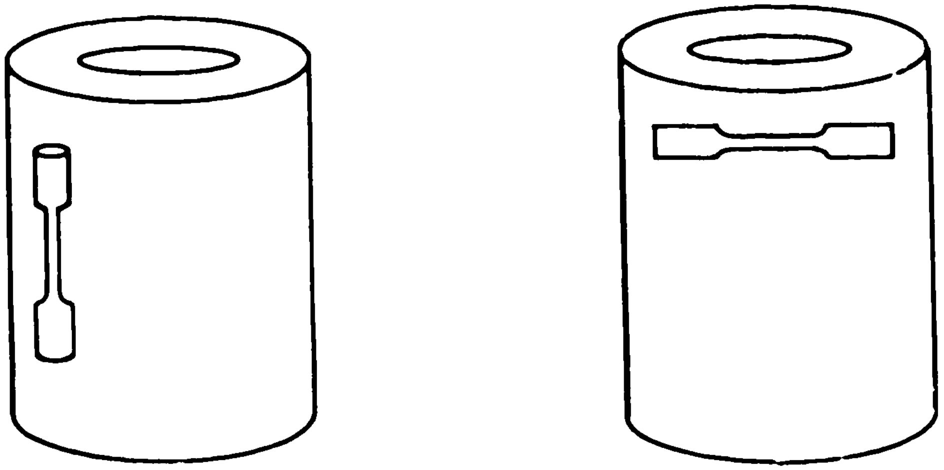
API Specification 5AC states that grade L-80 pipe must not be subjected to cold working after the final tempering treatment, except cold working which is incidental to normal straightening operations. Rotary straightening lengthens the tubular and constitutes an average plastic deformation of up to 0.5% permanent strain.[2] NACE standards contain a similar requirement limiting cold deformation to that incidental to normal machining operations such as rolling or threading.

Straightening processes are a significant source of residual stresses, along with the nonuniform cooling inherent to quenching operations.[12,18,21] Very high strength grades of casing, API C-90 and upwards, cannot be cold straightened without subsequent stress relieving. Hot rotary straightening at 500°C is used by some steel manufacturers to prevent internal stresses from being induced in the pipe.[49] Pipe straightened at the tempering temperature tends to remain straight and free from internal stresses after cooling.[18]

Cold work produces an anisotropic resistance to hydrogen embrittlement, with transverse samples failing much more quickly than longitudinal samples. (See Figure 1.1 for sample orientation from the tubular). Grains are elongated in the direction of working, and reduced in the other directions.[13] Cold deformation distorts the metal structure and increases the amount of hydrogen which can be contained in the metal.[23,25,42] The concentration of hydrogen in the metal is greatly enhanced by internal stresses and dislocations. Cold deformation increases the strength of the steel by raising the dislocation density and internal stresses.

High hoop stresses can be developed in standard threaded joints, so the pipe must possess good resistance to cracking in all directions.[3,11] These substantial hoop stresses are present mainly in collars not normally exposed to produced fluids. However leakage to the collars can often occur because of inadequate sealing at elevated pressures. Proprietary connections have been designed to minimize hoop stresses and improve sealing efficiency. This emphasizes the importance of low-stress premium connections for critical sour service production strings.[11,14,22]

The aim of this project was to determine the amount of cold work tolerable without creating SSC susceptibility in as-received and stress relieved L-80 steel. This is the basis for establishing a guideline to prevent SSC failures resulting from undesirable deformation. Simple hardness measurements are useful for monitoring the degree of cold work and can be correlated with SSC susceptibility. In practice, hardness measurements are feasible both before and after steel products leave the mill.



Longitudinal

Transverse

Figure 1.1 - Orientation of longitudinal versus transverse specimens.

2.0 EXPERIMENTAL PROCEDURE

2.1 Sample Preparation

Steel samples were cut from an API 5AC Grade L-80 seamless casing. The chemical composition of the steel tested is listed in Table 2.1. Spectrochemical analyses were performed to determine the chemical composition of the steel sample, although the chemistry and mechanical properties were also supplied by the steel producers. The casing had been austenitized at 870°C (1600°F), simultaneously water-quenched inside and outside, tempered at 688°C (1270°F) for approximately 66 minutes, and air cooled.

Hardness measurements were obtained with a Rockwell Hardness Tester, Model 4 TT BB. Rockwell B and C scales were used, depending on the degree of hardness increase with cold working. The B scale uses a 100 kg load with a 1.59 mm (1/16 in.) diameter ball indenter. A 150 kg load and conical "Brale" indenter are used for the C scale. Over 30 determinations across the wall thickness and from the outer surface of the casing were averaged to obtain the casing hardness value.

Tensile properties were determined with standard equipment and techniques (Table 2.2). (The yield strength apparently exceeds API 5AC L-80 restrictions, but this may be a result of machining the tensile specimens and their relatively small cross-section as compared with a full size casing or tubular). An Instron tensile machine, model TTD, with a maximum load of 88.96 kN (20,000 lb) was used. For tensile testing and cold deformation by tensile elongation, crosshead speed was set at 1.27 mm/minute (0.05 in./min.) and full scale load was set at 44.48 kN (10,000 lb).

All samples and tensile specimens were taken from one section of casing to obtain uniform chemical composition and metallurgy. This aids examination of the effect of a single variable, cold working, on SSC performance. Casing was used rather than tubing, so that sizeable tensile samples could be obtained.

The casing wall was cut longitudinally into strips before machining tensile specimens as shown in Figure 1.1. Several strips were given a second tempering heat treatment at 566°C (1000°F) for 30 minutes in a Harrop furnace, with an air environment. Temperature was controlled by a Data-Track programmer, Model 5500. The samples were cooled in air. Cylindrical tensile specimens, 6.4 mm (0.250 in.) in diameter by 25.4 mm (1.00 in.) in gauge length, were then machined carefully to avoid overheating and deformation. Before being immersed in the test solution, the samples were degreased in tetrachloroethylene, rinsed with acetone, and stored in a desiccator.

Cold working to 0, 5 and 9% plastic strain was accomplished by tensile elongation. This results in elongation distributed uniformly along the length of the specimen.[30] Strains greater than 9% result in nonuniform elongation, as the maximum load is reached and the specimen necks dow [illegible] ss values were determined for each degree of cold working by taking s [illegible] nents along the gauge length of as-received steel. For the case of stress re [illegible] steel, flat tensile coupons were machined, strained, and hardness evaluations obtained (Table 2.3).

2.2 NACE Constant Load Testing

Testing the steel for H_2S stress-cracking resistance was performed according to NACE Standard TM-01-77, "Testing of Metals for Resistance to Sulfide Stress Cracking at Ambient Temperatures," (Appendix 1). This test method describes test specimens, equipment, reagents, material properties and gives the test procedures to be followed. Metal specimens are stressed in uniaxial tension and immersed in acidified sodium chloride solution saturated with H_2S until they fail or 30 days have passed. This method is generally considered to be a severe accelerated test for SSC, although not recommended as a single criterion when evaluating an alloy for use in an H_2S environment.[34,57] CorTest proof rings were used for NACE constant load testing. Tensile stress is applied to the specimen by deflecting the ring, which is calibrated for load versus deflection and is supplied with a calibration curve. The load range of the rings is 0 to 689.5 MPa (100 ksi), based on a 0.640 mm (0.252 in.) gauge diameter specimen. This test unit is illustrated in Figure 2.1. The tensile specimen is completely immersed in an aqueous test environment contained in an acrylic environment chamber. Gases, supplied from pressurized cylinders, enter the environment through a flow tube into the test solution, and exit via a tube fitting flush with the chamber's top plate.

In this experiment, L-80 steel specimens were stressed to 90% of their yield strength which was previously determined by tensile testing (Table 3.1). This load is relatively severe, as it represents almost 110% of the specified minimum yield strength (SMYS), which is 550 MPa (80 ksi) for L-80 steel.

The standard NACE salt water solution was used: 5.0% sodium chloride, 0.5% acetic acid, in distilled water saturated with H_2S to approximately 3000 ppm (0.3%) H_2S. For the duration of the test, a continuous flow of H_2S gas was maintained through the solution. Solution pH was 3.5 to 4. All gases and chemicals used were reagent-grade purity.

A caustic absorbent solution for effluent gas was found effective in minimizing the amount of H_2S gas exhausted from the proof ring environment chambers. This solution consisted of 10% NaOH.

Electrical timers and microswitches were used to record time to failure. With failure of the specimen, the ring was released from its deflected state, clearing the microswitch and therefore stopping the timer. Specimens which did not fail in the 30 day test period were considered to be resistant to SSC.

2.3 SSRT Testing

Slow Strain Rate Technique (SSRT) testing involves the application of a relatively slowly increasing tensile stress to a specimen in a prescribed environment. Uniaxial loading is applied with a materials testing system (MTS), which basically consists of a fixed stiff frame, a carriage, a drive mechanism, and a load cell and recorder. The MTS available was a model 810, with a 25 tonne (27.6 ton) capacity load cell. Crosshead speed (or stroke control) was set at 13.3 mm

(0.525 in.) in 3.5 x 10^5 seconds (or 97.2 hr). Stroke control was set with an MTS 442 Controller and MTS 410 Digital Function Generator, using a ramp function. SSRT testing performed with the MTS was continued to failure in the standard H_2S-saturated NACE solution. Tensile specimens with the same gauge dimensions as those for the constant load testing were used. An extension rate of 2 x 10^{-6} s^{-1} applied for dynamic strain tensile testing. Load-time curves were recorded and maximum load was set at 55.6 kN (12,500 lb). Time to failure and elongation were determined from the recorded curves.

The SSRT has the advantage that the test is not terminated after an arbitrary time period, but always results in failure. Test time is considerably reduced as compared with static tensile tests.[22,24] Dynamic strain reduces the incubation period for crack nucleation and avoids the pitfalls associated with precracking, which is necessary with other SSC tests.[28] The SSC susceptibility is then related to the mode of fracture and other results such as time-to-failure and elongation. Metallography and fractography of SSC reveal a loss of ductility, brittle mode crack propagation, and secondary cracks perpendicular to the direction of applied stress. Data is obtained quickly by SSRT testing and is often used for screening purposes to compare SSC resistance of an alloy when only one parameter is varied.[24] Steels which exhibit SSC in this type of test may be acceptable in service if stresses are controlled, since the SSRT is a conservative test method.[35] No SSC in the test indicates no SSC failure should occur in actual service under the conditions tested.

An environment chamber similar to the CorTest chamber was constructed for use with the MTS. The test cell assembly was sealed off after saturating the solution with H_2S. Continuous bubbling of H_2S through the solution was deemed unsafe and unnecessary considering the short duration of each test (i.e. less than 6 hours). An enclosure was constructed to trap and vent any H_2S vapour escaping from the sealed test cell. PVC pipe was cut and hinged for an enclosure with easy access to allow attachment of the test cell to the MTS.

2.4 Fractography and Metallography

Cross sections of as-received and stress relieved steel were cut and mounted in thermosetting epoxy by compression molding for inspection with an optical microscope. Etching was then conducted with the following reagents: Nital, 5% nitric acid in ethanol; Picral, saturated solution of picric acid (5%) in ethanol; Vilella's reagent, 5 ml hydrochloric acid and 1 g picric acid in 100 ml ethanol (95%). Cross sections were examined with optical and scanning electron microscopy. Stress relieved samples were cut from the casing wall to observe all three dimensions, longitudinal, transverse and short transverse. Fracture surfaces were cleaned in a 3.5% HCl solution inhibited with 3% 2-butyne-1,4-diol, and were examined with optical and scanning electron microscopy. The SEM used was an International Scientific Instruments Model 60 (ISI-60).

Cross sections of specimens tested by both constant load and SSRT were inspected after H_2S exposure. Sections cut from the gauge length were cut longitudinally in halves, mounted, etched, and examined with both an optical microscope and an SEM.

X-ray detection analysis was used to determine the chemical cor[illegible]n of second-phase particles. The SEM high-energy electron beam striking the specimen surface produces characteristic X-ray emission by exciting the elements in the specimen. (Characteristic X-rays consist of discrete amounts of energy emitted from an atom when an electron jumps from the excited state back to its stationary state). X-ray signals are detected along with continuous background radiation, and are plotted as a spectrum, or range, of intensity versus energy (Figure 3.17). Light weight elements with atomic number below that of sodium cannot be detected by the energy-dispersive detector used, because of a lack of sensitivity. A Princeton Gamma-Tech, (PGT), System 4 microanalyser was utilized in conjunction with the SEM.

TABLE 2.1 Chemical Composition of L-80 Casing Tested, As Supplied and Comparison Analysis, Respectively (wt.%)

C	Mn	P	S	Si	Cr	Mo	Al	Ni	Cu
0.26	1.37	0.020	0.015	0.33	0.16	0.05	0.033	0.01	0.01

C	Mn	P	S	Si	Cr	Mo	Al	Ni	Cu	V	Sn
0.26	1.36	0.0205	0.014	0.33	0.17	0.055	0.0465	0.01	0.01	0.0015	0.001

TABLE 2.2 Mechanical Properties, As-Received and Stress Relieved Respectively

YIELD STRENGTH		TENSILE STRENGTH		ELONGATION (%)
MPa	ksi	MPa	ksi	
672	97.4	758	110	25.6
666	96.6	735	106.6	32

TABLE 2.3 Hardness Measurements

	COLD WORK % STRAIN	HRB*	HRC*
As-Received	0	97	18.7
	2	98	20.2
	5	99.4	22
	8	(101)	24
	9	(102)	25
Stress-Relieved	0	94	(14.2)
	5	94.5	(15.0)
	9	95.5	(16.0)

* Conversions between HRB and HRC are approximate

III. DESCRIPTION OF TEST UNIT

A. PARTS LIST

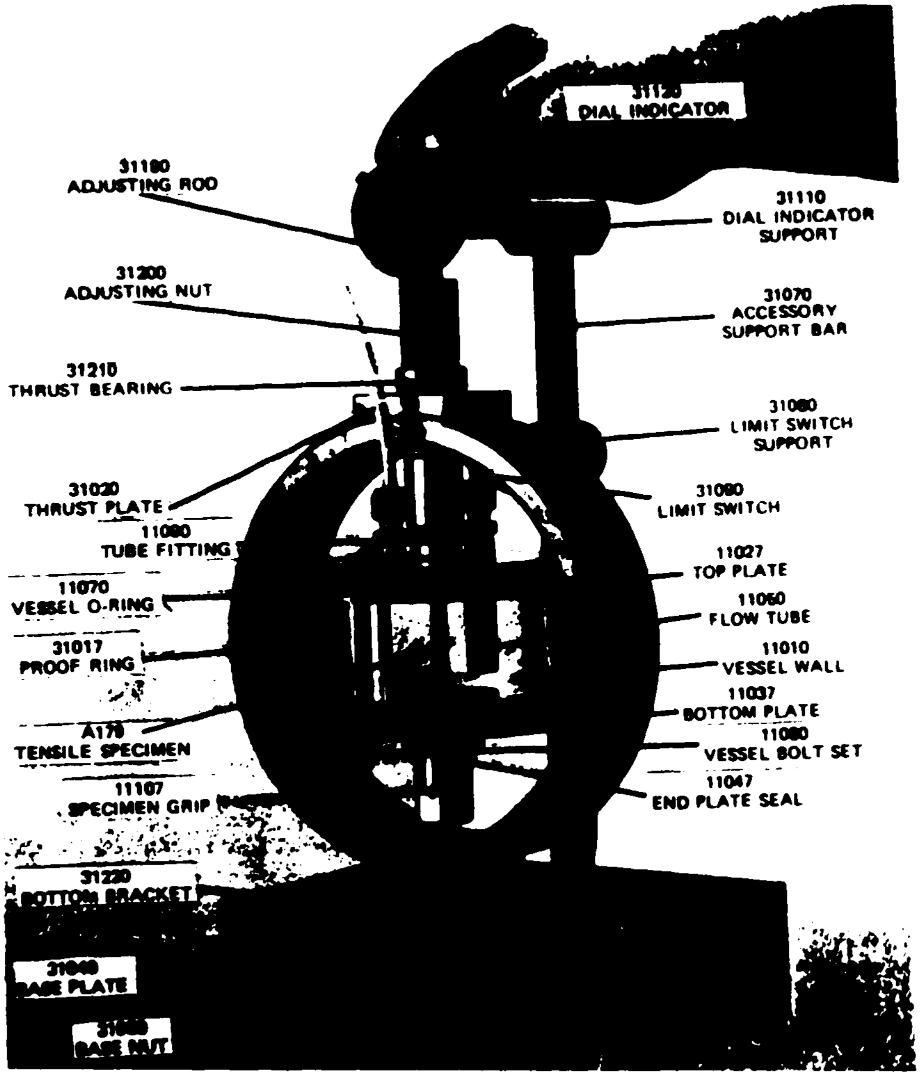


Figure 2.1 - CorTest proof ring assembly by permission of CorTest Incorpor
Willoughby, Ohio.

3.0 RESULTS AND DISCUSSION

3.1 Hardness Measurements

Hardness was found to increase with cold working, from 19 HRC (97 HRB) to about 25 HRC (102 HRB), in the as-received steels, as the degree of cold work increased from 0 to 9% (Table 2.3 and Figure 3.1). These values are only approximations, due to the difficulty of taking measurements on 6.4 mm (0.250 in.) diameter tensile samples, and due to conversions between Rockwell C and B scales (HRC and HRB).

Hardness values also increased with cold working of the stress relieved steel, with a range of 94 HRB (14 HRC) to 96 HRB (16 HRC) from no strain to 9% strain.

Only slight softening resulted from the stress relief. Coarsening of the iron carbides added to a drop in the steel's hardness, but was presumably offset somewhat by the secondary hardening effect of the alloy carbides. Chromium, molybdenum, and vanadium carbides require longer times for precipitation compared with iron carbides, and in sufficient quantities can raise a steel's hardness during tempering [23,30] With the relatively low alloy content of the subject steel, only a decrease in the rate of softening was observed.

It is important to note that the cracking resistance of a particular steel is governed by the microstructure, not the hardness per se. Hardness measurements were used in this experiment as a means of quantifying changes in the steel after stress relief and cold working. Industry standards use hardness limitations for sour service as it would be a complex problem to establish and apply a microstructural standard.

3.2 NACE Constant Load Tests

Time-to-failure data for each degree of cold working is presented in Table 3.1. Figure 3.2 depicts NACE constant load test results versus material hardness. It can be seen from this graph that the steel's susceptibility to SSC increases with hardness.

Specimens tested in the as-received condition with no cold working did not fail in the 30 day test period, nor after a further 4 days of exposure. Stress relieved specimens did not fail in the 30 day test period, regardless of whether or not they were cold worked. Thus L-80 steel in the as-received, unworked condition, or stress relieved with up to 9% strain by elongation was found resistant to SSC in acidic, aqueous H_2S, while loaded to stresses exceeding its specified minimum yield strength (SMYS) in this test series.

The shortest time to failure was with a sample strained to 9%. Variations in time to failure demonstrate the unpredictable nature of SSC. However, the data is sufficient to conclude that 5 to 9% strain by elongation greatly increases the probability of failure by SSC in an aqueous H_2S environment.

Specimens which failed by SSC in the SSRT tests, and in the NACE tests after 25 days, i.e. 600 and 648 hours, also exhibited cracking parallel to the applied stress (Figures 3.4 and 3.5). This form of cracking develops without an external stress and is called hydrogen induced cracking (HIC) or stepwise cracking. HIC normally propagates parallel to the rolling direction of the steel and depends strongly on the segregation of manganese and phosphorus in the ingot.[12] It is as complex as SSC and is controlled to a great degree by the same methods. HIC frequently occurs in association with SSC. By itself, this cracking process is usually observed in lower strength plate and pipeline steels with a yield strength not greater than 550 MPa (80 ksi). This experiment revealed a decrease in HIC resistance with cold working of the as-received metal.

3.3 SSRT Tests

As-received L-80 specimens were tested with this technique. All specimens exposed to the H_2S solution failed rapidly by deep SSC cracks, accompanied by a severe loss of ductility (Figure 3.6). Secondary cracks, also perpendicular to the applied stress, were seen along the gauge length. Little or no necking took place in the fracture region. By comparison, the specimen tested in air failed in a ductile manner with considerable reduction in area at the fracture surface.

With undeformed specimens, elongation to failure dropped from 24% in air to 3.8% in H_2S. Among all levels of cold working, fracture elongation ranged from 2.4 to 3.8% in H_2S, calculated from load-time curves. This range is attributed to data scatter, and is inconsequential when compared with the 24% elongation in air. No significant change in SSC resistance with increased cold working was detected with this test. SSRT test results are plotted in Figure 3.3 as load versus time to failure, the latter corresponding to elongation. This graph clarifies the lack of any reliable evidence of changing SSC performance with cold working by the SSRT test with the subject steel. Other SSRT experiments, also using a severe environment, have yielded a similar lack of conclusive results.[29]

Elongation is directly dependent on time, since the strain rate is set by the MTS crosshead displacement rate (Table 3.2). The very rapid failures during SSRT testing in H_2S may be due to the fact that dynamic strain testing maintains a driving force for slip-step emergence, and reduces the incubation period required for crack nucleation.[28,29]

To obtain more significant differences in SSC resistance from one amount of cold working to another, it may be necessary to employ a slower strain rate. A better recourse might be to greatly increase the degree of cold working. Flat tensile specimens would then have to be cold rolled, since tensile elongation past 9% strain results in nonuniform plastic deformation.

3.3 Metallography

A black iron sulfide film covered the surface of all samples examined. Generally, mild pitting and surface corrosion were noted, especially on samples that had been both cold worked and exposed in the NACE test cell for 25 to 30 days (Figure 3.5a). Pitting and surface corrosion were observed to be considerably less severe on undeformed steel specimens. No accurate measurements were taken but the trend was visually obvious.

Fine equiaxed, fully tempered lath martensite was observed in the as-received steel. Lath martensite consists of thin strips or laths grouped into packets or bundles. Each lath has a substructure of many dislocation cells, each cell containing a high density of dislocations.[7,39]

Stress relief had an observable effect on the microstructure. It is surprising to see extensive changes in microstructure during a stress relief, since normally after tempering at such a high temperature (688°C) one does not expect such a remarkable alteration in microstructure following a second tempering at a lower temperature (566°C). This suggests that the initial tempering treatment may not have been to the mill parameters specified. However, a less distinctive martensite lath structure was produced with more fully spheroidized carbides (Figures 3.20 and 3.21). There is a tendency for grains of ferrite to form as carbon precipitates from the martensite, as well as for cell walls and dislocations to disappear. However, discrete grains of ferrite could not be distinguished clearly in these micrographs. Microcracks associated with MnS inclusions became somewhat less sharp in appearance after stress relieving, (Figures 3.20b and 3.21). These microstructural changes are thought to have arrested crack initiation and/or propagation upon exposure to H_2S and a constant applied load.

MnS inclusions were randomly distributed, and surprisingly both spherical or slightly elongated. The latter were elongated in the steel's rolling direction, which was parallel to the direction of cold deformation. It follows that the inclusions were further elongated by cold working. Reportedly, room temperature sulphides invariably have a decohesive interface with the steel.[36] Thus voids are already present and available to trap hydrogen and enlarge before a load is applied.[8,41] Small voids or microcracks were found in the steel concomitant with the slightly elongated MnS inclusions (Figures 3.8 and 3.19).

Cold deformation may further increase decohesion of inclusion-matrix interfaces within the steel (Figure 3.9). However, further research is needed to predict the way that voids and inclusions react to cold working.[36]

Crack initiation and propagation are thought to be associated with microvoid formation and decohesion at the interfaces between inclusions and the matrix. Interfaces between the matrix and inclusions, carbides and other precipitates have been documented as powerful trap sites for hydrogen.[8,43,49,53] High stress concentrations can readily develop at these interfaces because of the elastic-plastic incompatibility between the tougher iron matrix and essentially brittle precipitates. The combination of hydrogen and high stress concentrations, especially after cold deformation, can augment decohesion of the interfaces and initiate cracking. Although decohesion and microcracking may also have occurred at carbide and other precipitate interfaces with the matrix, the effects of these are felt to be insignificant in comparison with the effects of MnS inclusion interfaces. This conclusion is based on the finer size of the carbide particles as compared with the MnS inclusions, along with the more uniformly spherical shape of the carbides.

X-ray analysis was used to identify the MnS globules (Figure 3.17). Several spherical MnS inclusions appeared to be associated with spherical iron oxide inclusions, although oxygen cannot be identified by the X-ray analysis equipment utilized (Figure 3.18). However, surface energy would be lowered by the conglomeration.

Undissolved carbides approximately 0.1 to 0.4 micrometers (microns) in diameter tended to be segregated to martensite lath boundaries and prior austenite grain boundaries (Figures 3.7). Stress relieving the steel made the carbides increasingly spherical in shape, fewer in number and slightly larger (Figures 3.20a and 3.21b). With recovery or recrystallization of the martensite, iron carbides are usually located at ferrite grain boundaries.[39] As tempering progresses, the distribution of carbides is reported to become more random, compared with the linear arrays seen along lath and prior austenite grain boundaries. In the present investigation however, this difference was not particularly obvious between the single and double tempered steel. No cracked carbides were seen in the steel tested as the sulphide inclusion content would have to be extremely low before carbides would begin to affect the steel's ductility. High strength steel alloys with low sulphur contents (less than 0.01%) depend on carbides being randomly distributed and spherical for SSC resistance.[8,31,43]

The mechanisms of this second temper, stress relieving heat treatment are thought to be thermally induced dislocation movement, diffusion, and some recrystallization. Internal strains were thus reduced significantly. Also, retained austenite, which had transformed to martensite, was tempered. The combined effect was to reduce the brittleness of the steel and improve its SSC resistance.

3.5 Crack Morphology

SSC cracks were generally transgranular with very little branching (see representative micrograph, Figure 3.10). Separate cracks often initiated in several places on the surface of the tensile samples. Crack propagation was normal to the tensile stress. Fracture occurred by mechanical failure when the metal remaining between the cracks was torn apart (Figure 3.11).

No inclusions concomitant with primary cracking could be detected by SEM, optical microscopy or by X-ray analysis.

HIC occurred to varying extents in the cold worked as-received, constant load NACE test specimens. This type of cracking can propagate in the direction parallel to the tensile stress (Figure 3.4). The most severe occurrence was observed with a NACE test of a 9% plastically strained specimen (Figure 3.5).

HIC appears to have initiated at a sulphide stringer inclusion, although no positive confirmation of inclusion chemistry could be made. The occurrence of HIC in a high strength steel suggests a large fraction of hydrogen in the steel, (a high H fugacity).[9,48,52,54]

3.6 Fractography

SSC fracture surfaces reveal both brittle and ductile modes of failure (Figure 3.12). Typical transgranular quasi-cleavage brittle mode was seen on samples cold worked to 9% strain. With decreasing amounts of cold working, the hydrogen fracture surfaces became less brittle in appearance (Figure 3.13). It is interesting that the microcracks look blunt and rounded with no cold work, whereas they appear quite sharp on the cold worked specimens. In contrast, the ductile overload surfaces show microvoid coalescence (Figure 3.14). Thus failure began by brittle cracking and finished by ductile overload.

The brittle fracture surfaces were often flat semi-circular zones for which the crack initiated on the outer surface of the gauge section (Figure 3.12). One specimen had a flat circular zone that originated from internal crack initiation (Figure 3.15). Flat voids across the fracture surface are formed by hydrogen collecting around inclusions, leading to the development of very large voids.[10]

Cracking was prevalently transgranular. This tends to indicate that impurity elements in the steel have not segregated excessively to grain boundaries.

TABLE 3.1 SSC Test Results by the NACE Tensile Test

	COLD WORK % STRAIN	SAMPLE	TIME-TO-FAILURE HOURS *
As-Received Applied Stress 605 MPa (87.7 ksi)	0	1 2	N/F N/F
	5	1 2	N/F 600
	9	1 2 3	N/F 16 648
Stress-Relieved Applied Stress 599 MPa (86.9 ksi)	0	1 2	N/F N/F
	5	1 2 3	N/F N/F N/F
	9	1 2 3	N/F N/F N/F

* N/F signifies sample did not fail in the 720 hour test period

TABLE 3.2 SSC Test Results by the Slow Strain Rate Technique (SSRT)

COLD WORK % STRAIN	SAMPLE #	TIME-TO-FAILURE HOURS	TIME-TO-FAILURE MINUTES	AVERAGE HOURS	AVERAGE MINUTES	ELONGATION TO FAILURE %
0	1	4	40	4	47	3.8
	2	5	12			
	3	4	30			
5	1	2	40	3	5	2.4
	2	3	30			
8	1	4	10	4	32	3.6
9	1	5	37			
	2	3	48			
0	Air Test	31				23.8

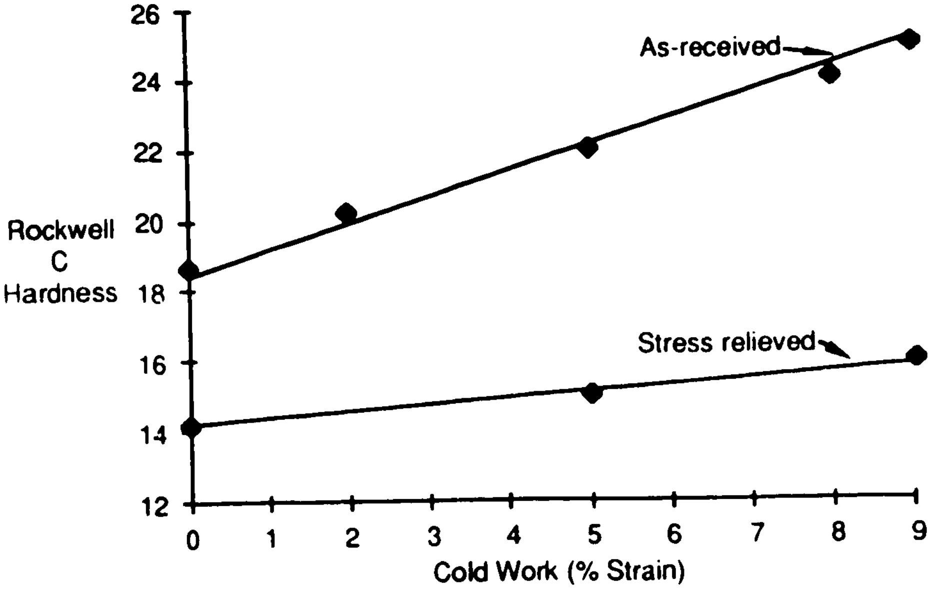


Figure 3.1 - Calibration of Rockwell hardness numbe[illegible] cold work by percent plastic strain.

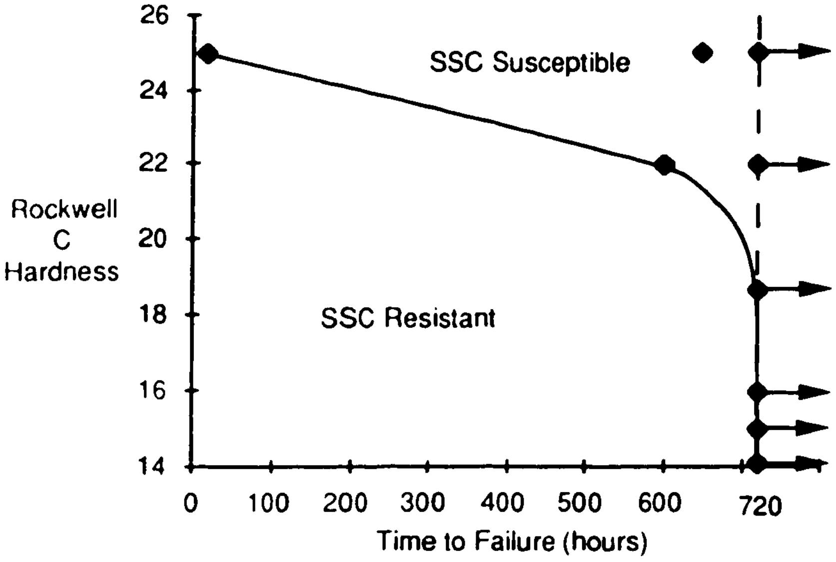


Figure 3.2 - NACE constant load test results as time to failure versus material hardness. Above a certain combination of hardness and exposure time, SSC failure is a definite possibility. Note that 720 hours corresponds to the 30 day test period, at which point the metal is considered resistant to SSC.

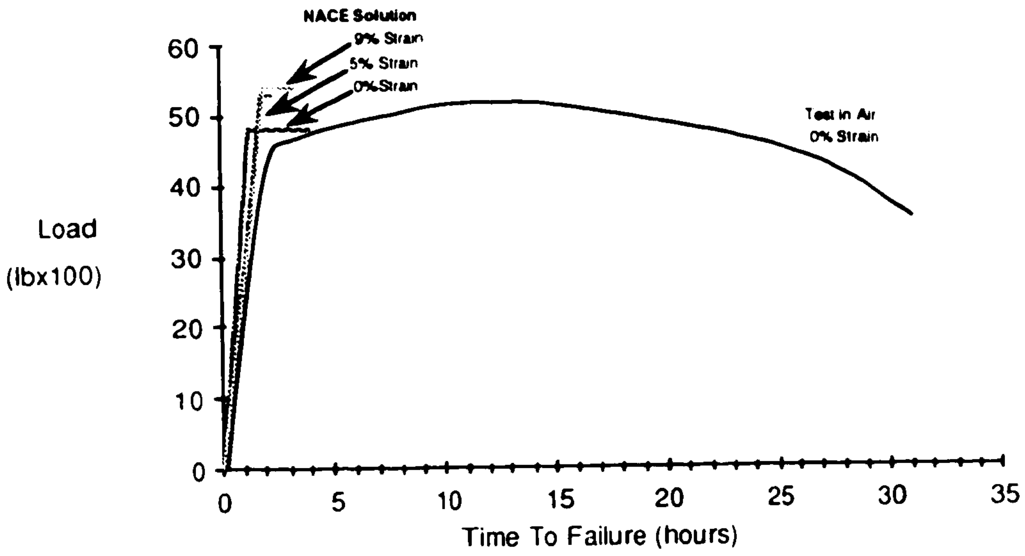


Figure 3.3 - Slow strain rate technique (SSRT) test results show the dramatic decrease in time to failure (and correspondingly elongation) with use of the NACE test solution. However, insignificant differences between specimens cold worked to different degrees were obtained with NACE solution tests.

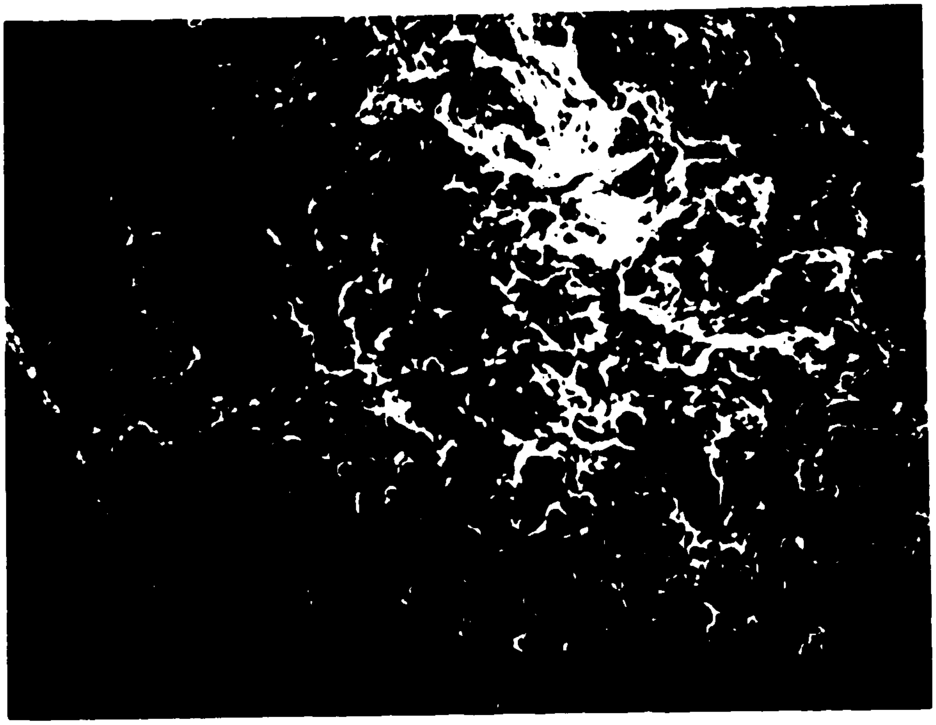


Figure 3.4 - HIC crack seen propagating normal to the SSC fracture surface and into the plane of the applied stress (0% cold work, SSRT sample, SEM 110 x magnification).

3.5 a)

3.5 b)

Figure 3.5 - Most severe case of HIC seen in a 9% plastically strained sample which failed following 27 days exposure in the NACE test.

a) Side view, with pitting visible (6.4 x magnification)

b) Dark crevasse extending into fracture surface is the HIC crack, (SEM, 11 x magnification).

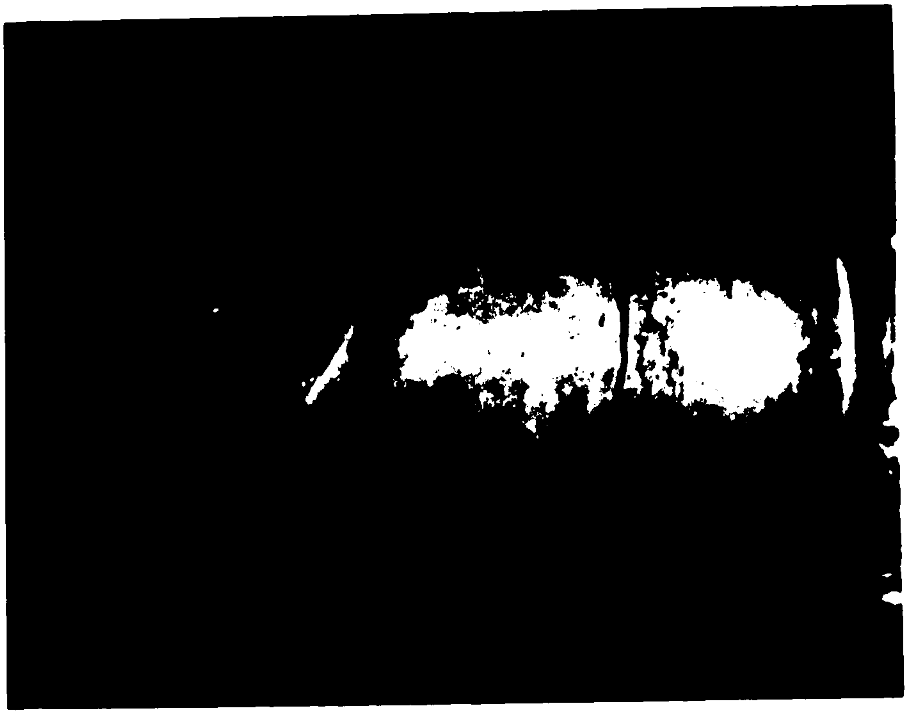


Figure 3.6 - SSC fracture and secondary SSC crack on gauge length, (0% cold work, SSRT sample 6.4 x magnification).

3.7 a) 1700 x

3.7 b) 4900 x

Figure 3.7 - Carbides in tempered martensite (SEM).

Figure 3.8 - Microcracking associated with an elongated MnS inclusion, in a 9% cold worked sample after NACE test lasting 27 days, (cross-section, 960 x magnification).

Figure 3.9 - Microcracking and inclusion morphology in 9% cold worked sample after NACE test lasting 16 hours, (cross section, 900 x magnification).

Figure 3.10 - SSC cracks propagating in a specimen cold worked to 9% strain and exposed to the NACE test for 26 days. Sample failed at these cracks the following day. (Sample surface, 40 x magnification).

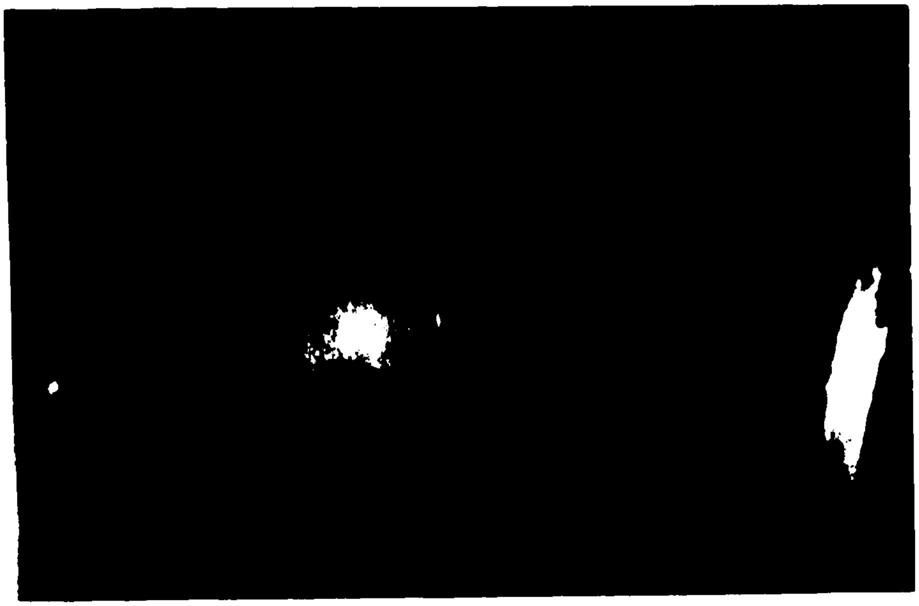


Figure 3.11 a) - Several SSC cracks normal to tensile axis, joined by mechanical overload at failure, (9% cold work, SSRT sample, 6.4 x magnification

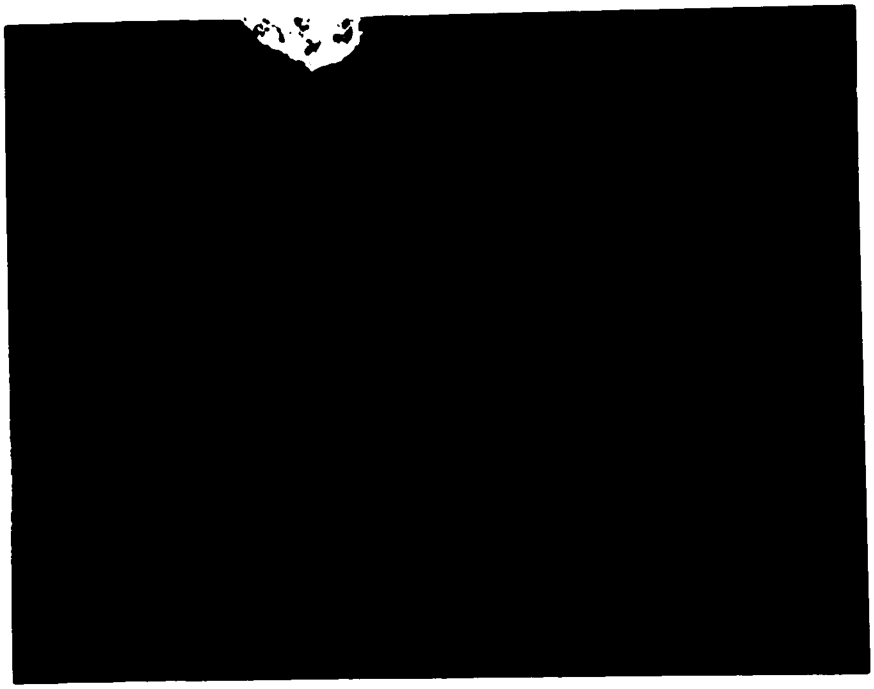


Figure 3.11 b) - Fracture surface revealing SSC cracks as distinct flat plateaus.

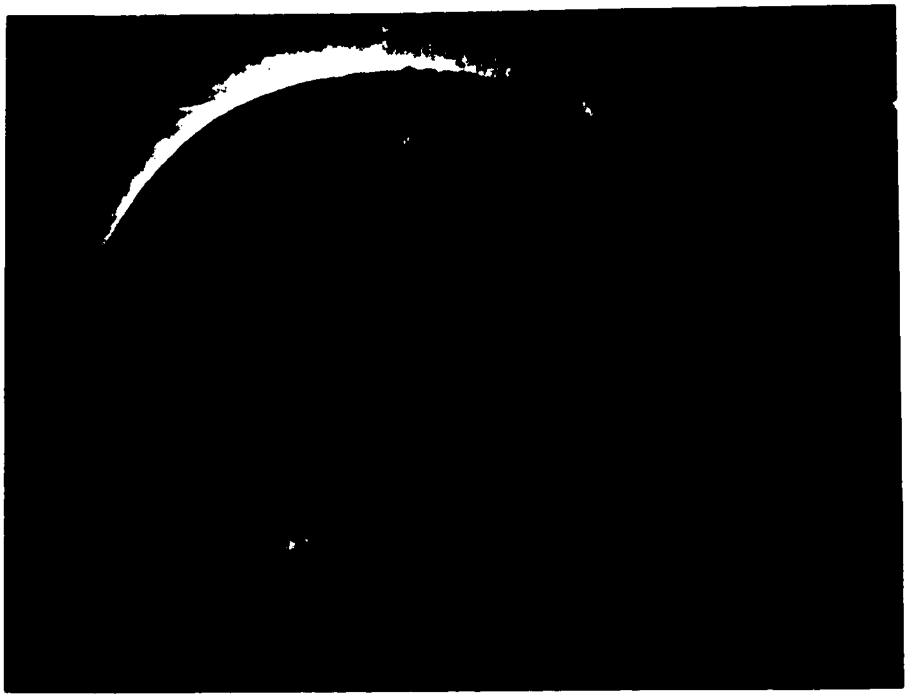


Figure 3.12 - Darker flat areas on outer surfaces are brittle, SSC fracture surfaces. Lighter, rough areas are ductile overload surfaces (9% cold work, SSRT sample, SEM 11 x magnification).

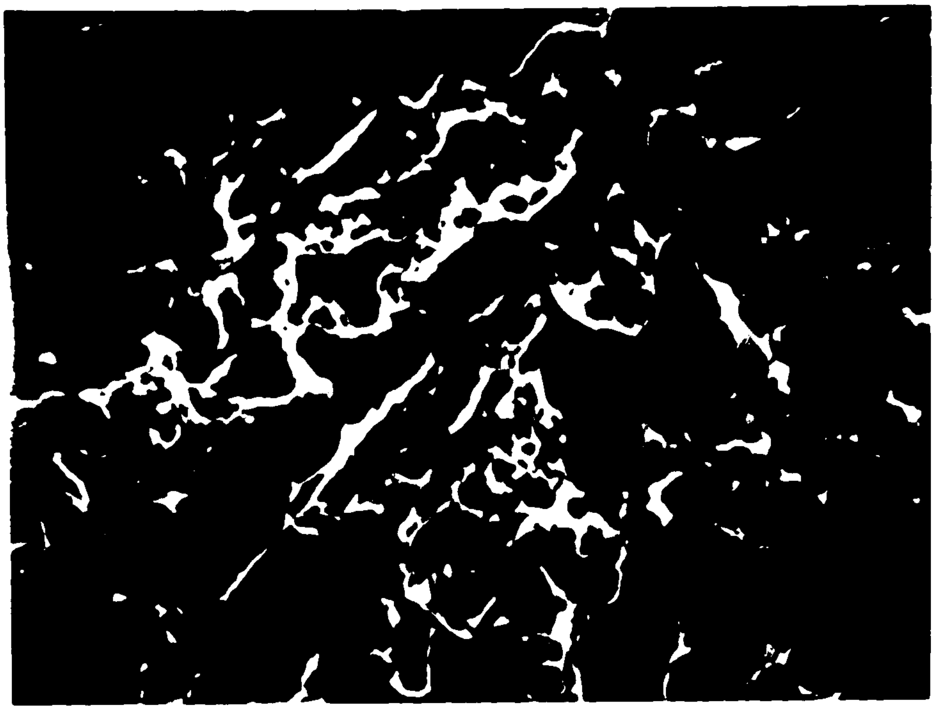


Figure 3.13 a) - Brittle, quasi-cleavage fracture surfaces, (SEM, 1100 x magnification).

a) 9% cold worked sample.

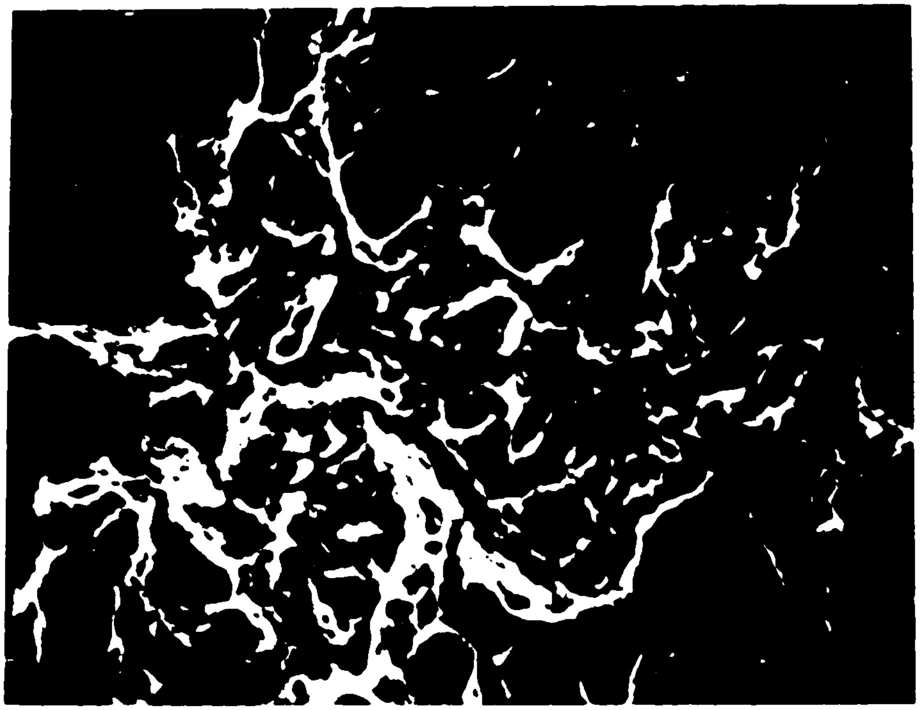


Figure 3.13 b) - 5% cold worked sample.

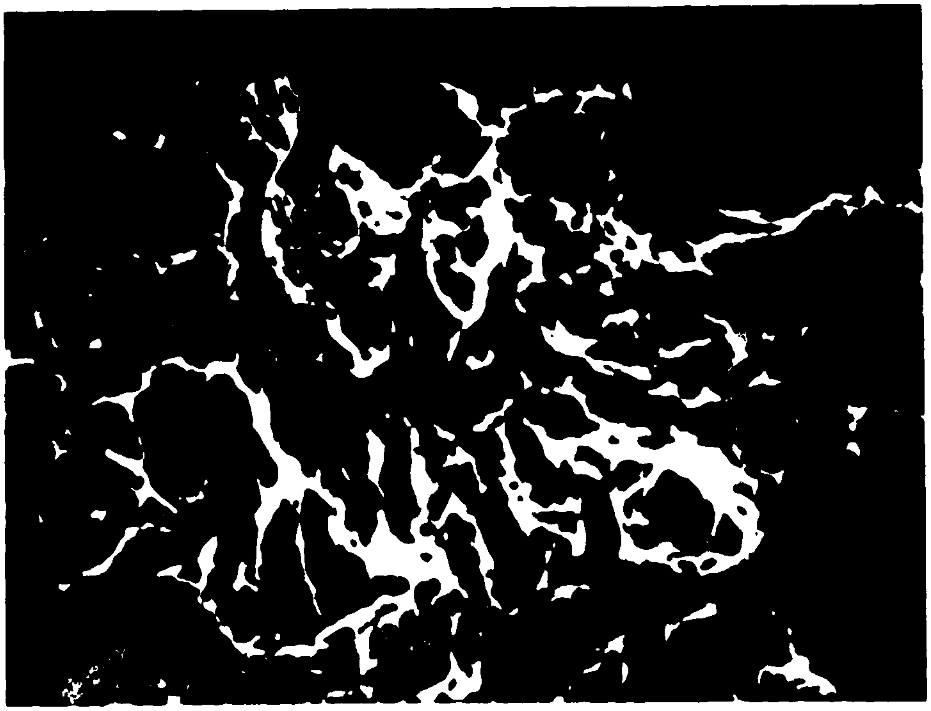


Figure 3.13 c) - Unworked sample.

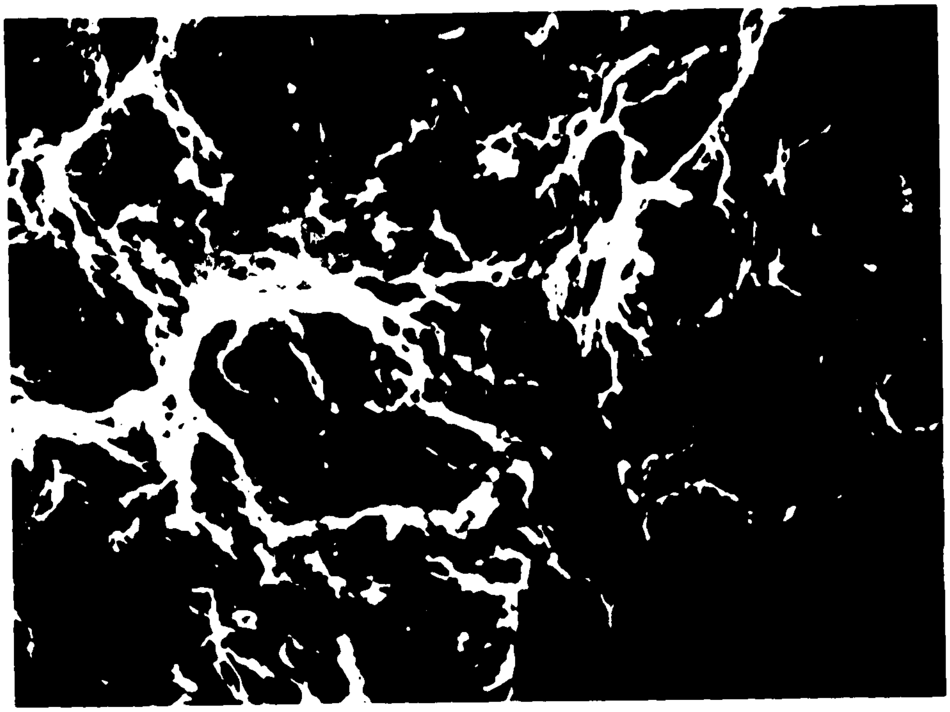


Figure 3.14 a) - Ductile-dimple fracture surfaces. Dark regions are microvoids and light regions are last strands of steel broken upon failure, (SEM, 1100 x magnification).

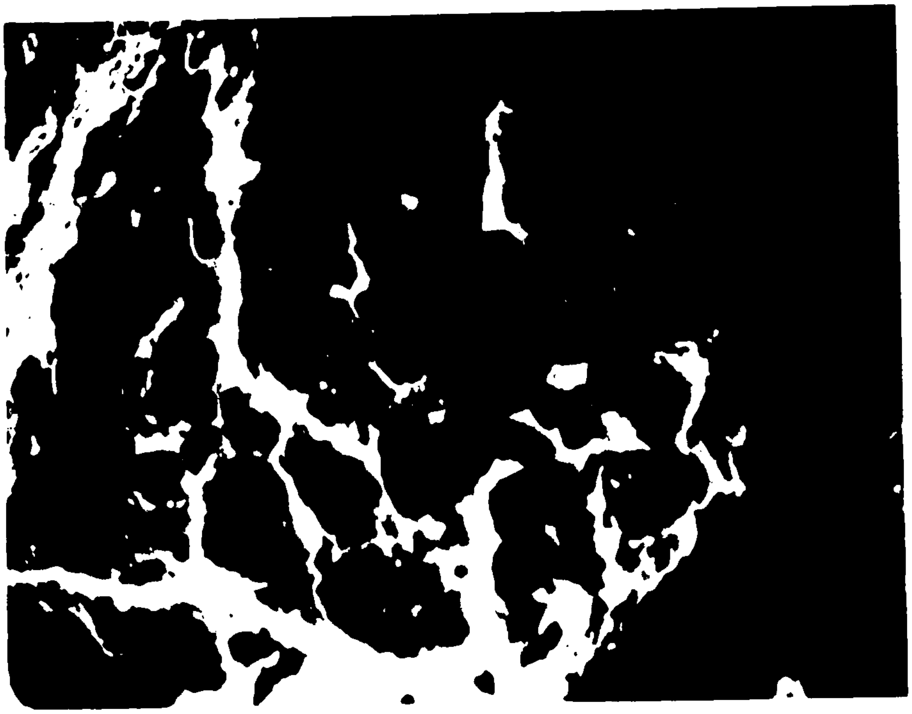


Figure 3.14 b) - Minuscule white particles are carbides, (SEM, 3400 x magnification).

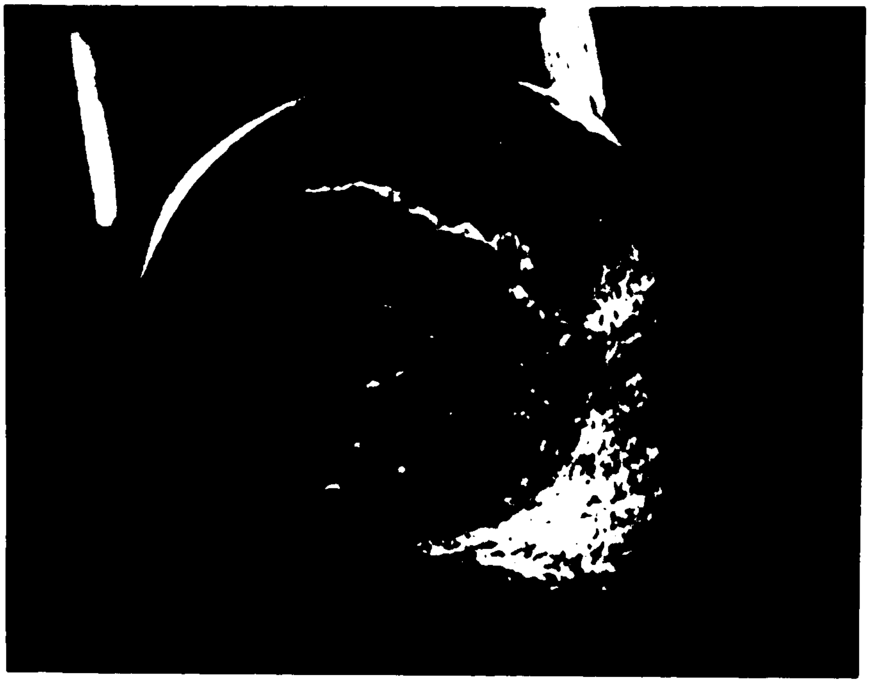


Figure 3.15 - SSC crack initiated at centre of flat circular zone, as seen on left side of fracture surface, (SEM, 11 x magnification).

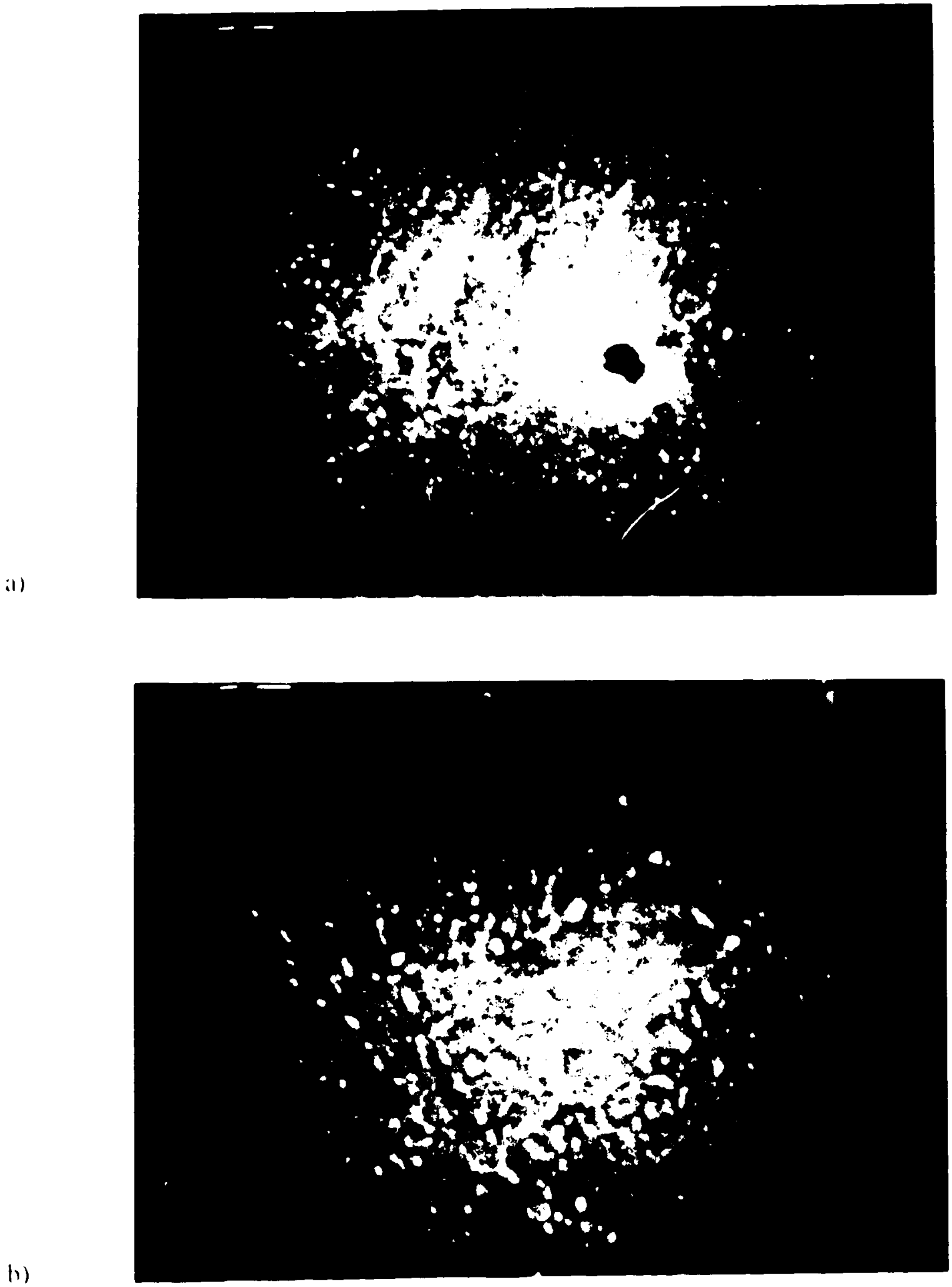


Figure 3.16 - Carbides in double temper stress-relieved martensitic steel, (SEM).

a) 3400 x b) 4900 x

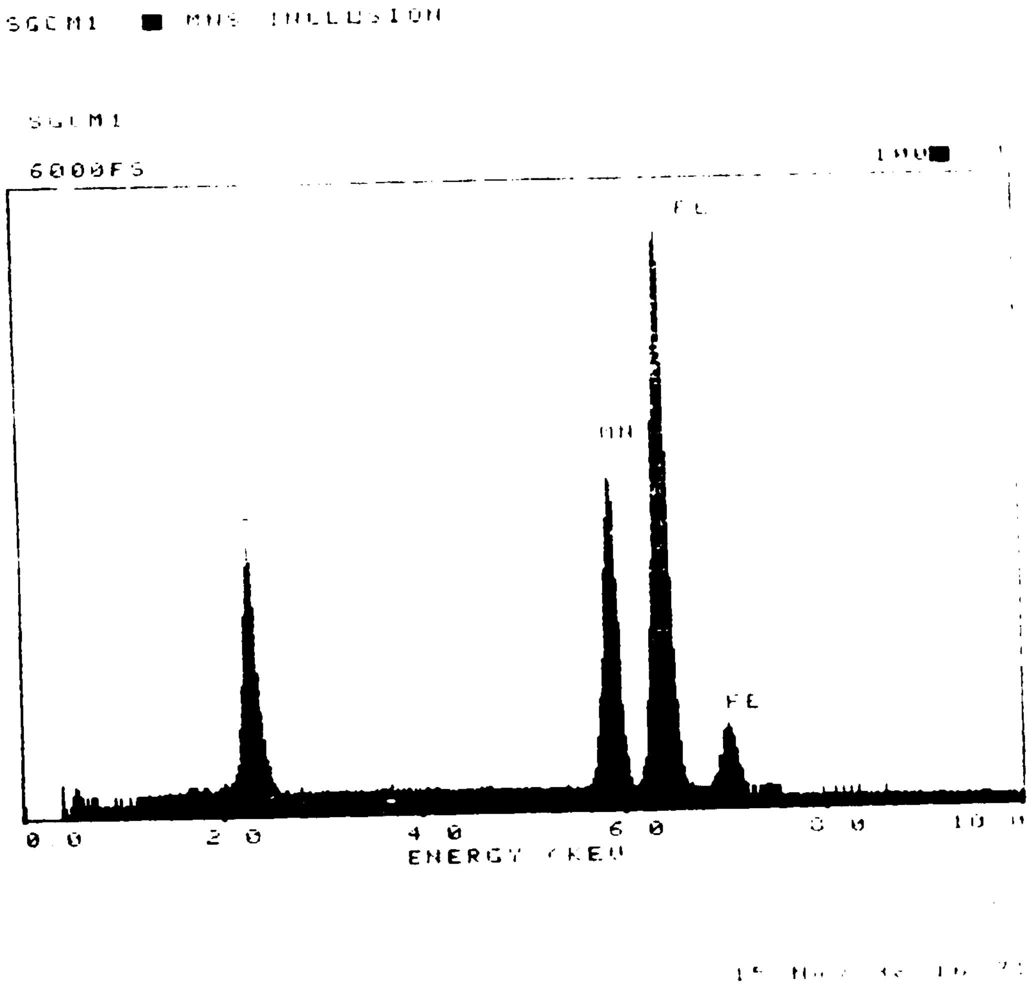


Figure 3.17 - X-ray spectrum analysis identifying a typical MnS inclusion.

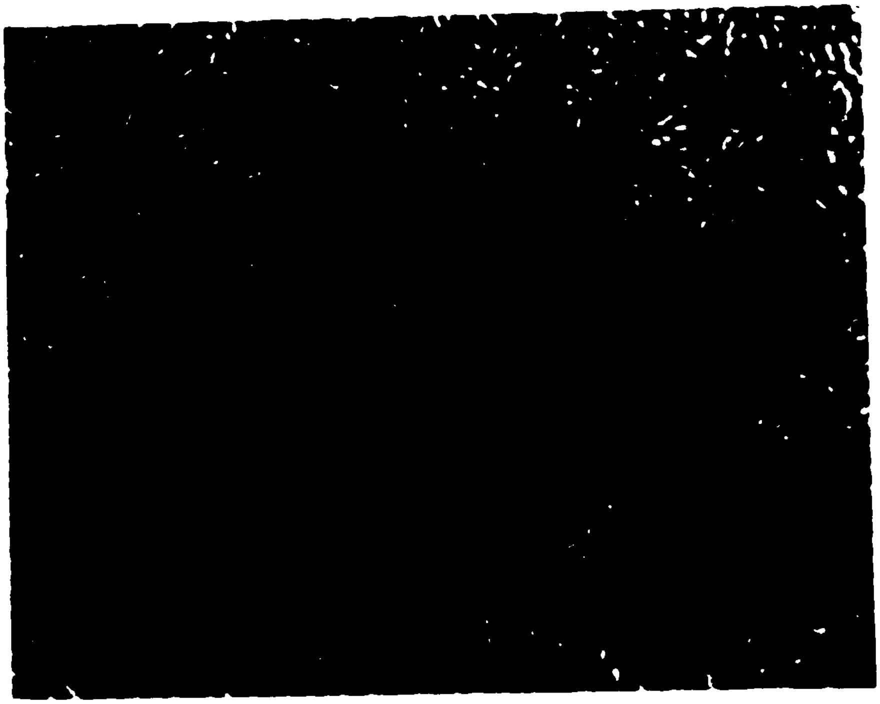


Figure 3.18 - Spheroidized MnS inclusion associated with another inclusion, presumably an iron oxide, in stress relieved martensitic steel (960 x magnification).

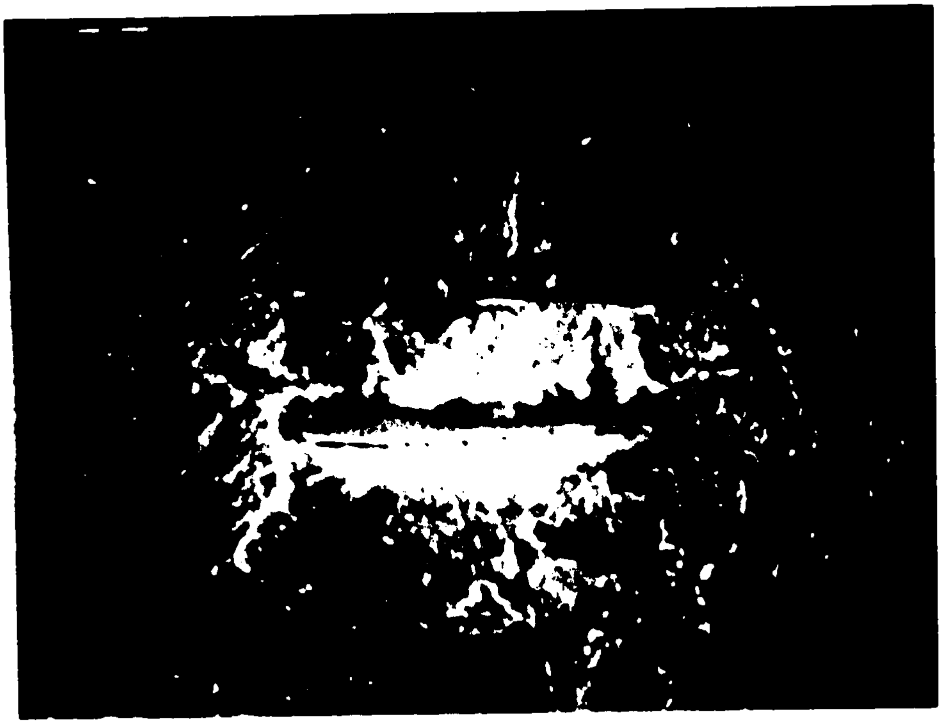


Figure 3.19 - Slightly elongated MnS inclusion with decohesion at the matrix-inclusion interface, as-received steel (SEM, 3400 x magnification).

Figure 3.20 - As-received L-80 steel; tempered martensite microstructure (960 x magnification).

a) Spherical MnS inclusion.

Figure 3.20 b) - Typical elongated MnS inclusion.

Figure 3.21 - Stress relieved L-80 steel; microstructure of tempered martensite with some recrystallization and spheroidized carbides, (960 x magnification).

a) Transverse cross section.

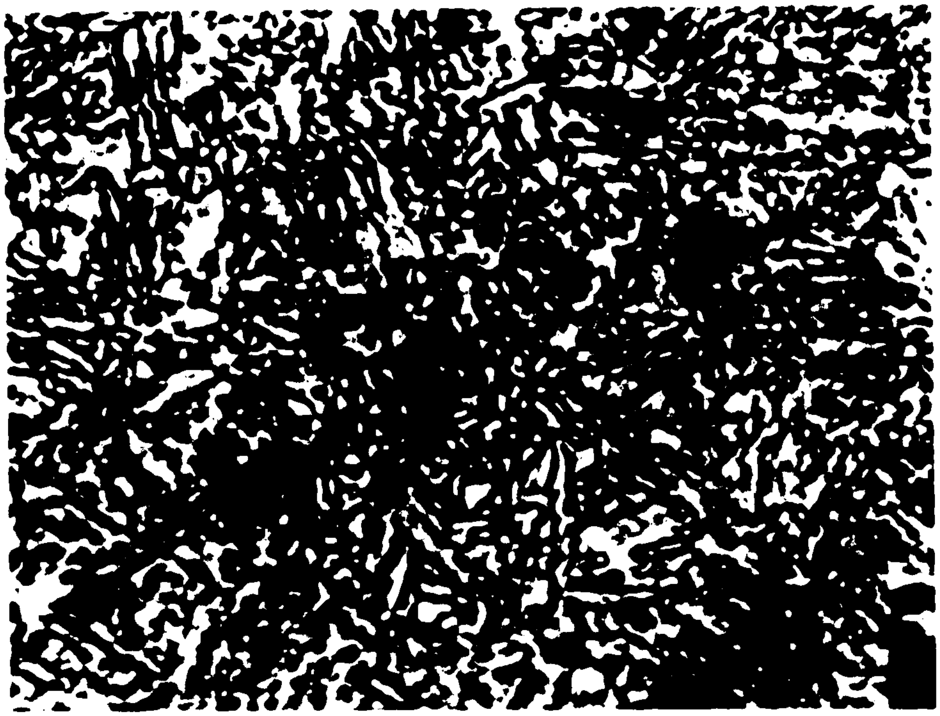


Figure 3.21 b) - Longitudinal cross-section.

Figure 3.21 c) - Short-transverse (or longitudinal through-thickness) cross-section.

4.0 CONCLUSIONS

1) Cold deformation decreased SSC resistance and hydrogen-induced cracking resistance of the as-received L [illegible] after only 5% plastic strain. This behaviour was found using the [illegible] constant load test with an applied stress of nearly 110% of the specified minimum yield strength (SMYS). A correlation was obtained between increases in hardness and deterioration of SSC resistance. As received, the unworked L-80 steel passed the SSC test (when loaded uniaxially to more than 100% of the SMYS). As well, the unworked steel appeared to be more resistant to pitting and surface corrosion.

2) As the degree of cold work was decreased, SEM investigation revealed a change in brittle fracture mode, from typical quasi-cleavage to a more ductile fracture. Increases in brittleness of the steel result from cold deformation which augments hydrogen embrittlement, as well as raising internal stresses in the crystal lattice.

3) The slow strain rate testing technique produced rapid failure in all samples tested. This behaviour can be attributed to the similarity of the steel samples and to the severity of the NACE solution.

4) Double temper stress relief improved SSC resistance of the subsequently cold worked L-80 steel. All stress relieved specimens passed the NACE constant load test, including those specimens cold worked to 5 and 9% strain. With stress relief, the microstructure changed from a pronounced martensite lath structure with a high proportion of spheroidized carbides into a less distinct, partially recrystallized structure with a larger proportion of well-spheroidized carbide particles. Microcracks and separated inclusion matrix interfaces became less sharp. The difference in SSC resistance, particularly after cold working, can be explained by the dramatic changes in microstructure and inclusion morphology imparted by stress relief heat treatment.

5) Hardness of this steel rose from an initial state of approximately 18.7 HRC (97 HRB) in the as-received condition, to 25 HRC (102 HRB) at 9% plastic elongation. The maximum hardness of 22 HRC recommended by NACE corresponds to about 5% cold work and, in this test series, was associated with SSC susceptibility. Stress relief by a second tempering treatment reduced the hardness to 14.2 HRC (94 HRB), which was raised to 16 HRC (95.5 HRB) with 9% strain. It appears there may be a certain advantage to stress relieving L-80 steel that will be subsequently cold worked and exposed to aqueous H_2S. Further research is indicated to statistically prove this result, and to confirm similar behaviour with L-80 grades from several manufacturers.

5.0 RECOMMENDATIONS

1) There is a need to investigate the extent of cold working experienced by tubulars in service. If experimental amounts of plastic deformation were correlated with cold work incurred after single or double tempered steel tubulars leave the mill, better quantification of the relationship between hardness increases and corresponding changes in SSC resistance could be obtained. To relate laboratory cold work deformations to the potentially larger values experienced in field practice would require an increase in the extent of experimental deformation. This could be achieved by cold rolling flat tensile specimens, rather than by utilizing elongation which is characterized in L-80 steel by non-uniform deformation after 9% strain. Also, the SSC resistance of steel previously cold worked to different degrees could be quantified by determining the threshold stress, which is defined as the limiting amount of stress that can be applied without producing SSC failure of the steel.

2) Cold work could be expanded to include elongation, compression, and torsion, since all three modes of plastic deformation are associated with cold working of tubulars in service. The SSC resistance of cold worked, welded tubulars or higher strength steel such as C-95 and P-110 should also be investigated, as these steels are in use in petroleum production. The higher strength steels tend to be more susceptible to SSC than L-80, which may prevent their use in severe downhole environments.

3) Most SSC tubular failures in the petroleum industry occur at or near couplings. High hoop stresses often develop in standard threaded connections, so good resistance to cracking in the longitudinal direction is necessary. To investigate the directional SSC resistance of tubulars, tensile samples should be cut from the pipe wall transversely and tested. Results could then be compared with the performance of longitudinal samples that have been tested in this project. Threaded couplings can also fail as a result of SSC cracks initiating at the root of a thread. Tests could be performed to

evaluate SSC resistance of threaded or notched tensile samples, with particular attention to the residual stress concentration and microstructural deformation at the root of the thread. Other field service conditions not considered herein may contribute further to SSC susceptibility.

4) As a direct extension of this project, it would be worthwhile to obtain improved quantification of the degree of cold work tolerable for a single tempered L-80 steel exposed to aqueous H_2S. SSC testing could be performed at narrower increments of cold work, say 2, 4 and 6%. Also, if applied tensile stresses were reduced to less than the SMYS, more than 5% cold working may be required to cause SSC susceptibility in the as-received steel. To determine the amount of cold deformation necessary to produce SSC failure in the stress relieved L-80 specimens, the extent of deformation would have to be increased.

5) Another area for consideration is the significance of microcracking changes occurring as the degree of cold deformation increases, and their effect on SSC performance. The degree of deformation also affects the behaviour of inclusions, voids and microcracks. These phenomena could be examined to better understand their effect on SSC fracture.

6) Evaluation of steel performance in sour environments could be expanded to include other high strength steel fabrication parameters. In particular, rapid cooling after the first or second tempering treatment may further improve SSC resistance of the L-80 alloy.

7) Another potentially productive research topic is the effect of cold work on pitting and surface corrosion rates. Pitting may initiate SSC, and tends to be more severe when CO_2 is present. CO_2 is recognized as an important corrosive agent and is often found along with H_2S in petroleum recovery.

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APPENDIX 1

TEST METHOD

technical practices committee

NATIONAL ASSOCIATION OF CORROSION ENGINEERS

NACE

NACE Standard TM-01-77

Test Method

Testing of Metals for Resistance to Sulfide Stress Cracking at Ambient Temperatures

This NACE Standard is subject to mandatory review within two years of issue and can be revised at any time if warranted. Comment on this Standard from any source is invited by the Association.

Approved July, 1977
National Association of Corrosion Engineers
P. O. Box 1499
Houston, Texas 77001
713/622-8980

Foreword

Sulfide stress cracking (SSC) failures of metals exposed to hydrogen sulfide containing oil field environments have been recognized as a problem for almost 25 years. Both laboratory and field data have shown that concentrations of a few parts per million of hydrogen sulfide may be sufficient to lead to SSC failures. Laboratory and field experiences have allowed engineers to select materials having minimum susceptibility to SSC. Though the remainder of this Standard will be focused on SSC failures, other failure modes such as corrosion fatigue, general corrosion, etc., can be the cause of failure in sulfide environments.

During the last few years, the need for better understanding of the variables and better correlation of data have become apparent for several reasons. New design requirements call for higher strength alloys, which in general are more susceptible to SSC than the lower strength alloys. These design requirements resulted in extensive developmental programs to obtain more resistant alloys and/or heat treatments. At the same time, users in the petroleum industry are pushing present materials much closer to their physical limits. Attempts to use higher strength steels in other industries have occasionally resulted in SSC failures.

SSC failures are generally thought to result from hydrogen embrittlement. When hydrogen atoms are cathodically evolved on the surface of a metal (as by corrosion or cathodic charging), the presence of hydrogen sulfide (and a few other compounds containing cyanides, arsenic, etc.) tends to cause hydrogen atoms to enter the metal rather than form hydrogen molecules which do not enter the metal. In the metal, hydrogen atoms diffuse to regions of high triaxial tensile stress or some microstructural configurations where they become trapped and increase the brittleness of the metal. Though there are several kinds of hydrogen damage to metals, delayed brittle fracture of metals due to the combined action of corrosion in a sulfide environment and tensile stresses (which may be well below the yield stress) is the phenomenon that is known as sulfide stress cracking.

These and other considerations led NACE Unit Committee T-1F on Metallurgy of Oil Field Equipment to establish Task Group T-1F-9 (Metals Testing Techniques for Sulfide Corrosion Cracking) with the assignment to prepare a NACE Test Method Standard pertaining to testing of metals for resistance to sulfide stress cracking. Task Group T-1F-13 was established to verify that the T-1F-9 Test Method was reproducible between different laboratories. Originally, this Test Method contained a notched beam as well as the smooth tensile specimen. Task Group T-1F-13 recommended standardization of the tensile test but not the notched beam test. Further work is indicated with different types of beam and fracture mechanics specimens for possible inclusion at a later date. Task Group T-1F-17 has been established to accumulate data of interest to NACE conducted with the tensile test as described in this Standard.

This Test Method, issued by the NACE Group Committee on Corrosion Control in Petroleum Production (T-1), is directed toward testing of metals for resistance to cracking failure in aqueous environments containing hydrogen sulfide. It must be emphasized that the sole purpose of the Test Method is to facilitate conformity in testing so that data may be accumulated from different sources and compared on an equal basis. Evaluation of the data requires judgment on several difficult points which must remain a matter for the individual user or other specific groups and situations. It has been noted that stress corrosion testing is a difficult task. This Test Method is generally conceded to be a severe, accelerated test for SSC, making the evaluation of the data extremely difficult. In testing the reproducibility of this Test Method among different laboratories, several undesirable side effects, natural with any accelerated test, were noted.

1 The test environment may cause failure by hydrogen blistering as well as SSC. This is especially true for lower strength steels not usually subject to SSC. The presence of a blistering form of failure may be detected by metallographic observation.

2 The test environment may cause corrosion for some alloys which normally do not corrode in actual field service and thereby induce SSC failures in alloys which ordinarily do not fail by SSC. This problem is especially acute with stainless steels.

In summary, this Test Method is an accelerated test for SSC and may also produce failures by other modes. It should not be used as a single criterion for evaluating an alloy for use where hydrogen sulfide or other hydrogen charging situations occur. Attention should be paid to the other factors which may strongly influence SSC such as pH, temperature, H_2S concentration, corrosion potential, stress level, manufacturing considerations, bimetallic effects, etc., as well as prior field experience and safety considerations when attempting to judge the suitability of a metal for use in a specific situation.

Section 1: General

1.1 This Test Method is concerned with the ambient temperature testing of metals subjected to tensile stresses for resistance to cracking failure in low pH aqueous environments containing hydrogen sulfide.

1.2 This Test Method gives recommendations on the reagents to be used, describes the test specimens and equipment to be used, discusses base material and specimen properties, and gives the test procedures to be followed. Reporting of the test results is also discussed. The test procedure can be summarized as follows: Stressed specimens are immersed in acidified sodium chloride solution saturated with hydrogen sulfide at ambient pressure and temperature. Applied stresses at convenient increments of the yield strength can be used to obtain sulfide stress cracking data. Time-to-failure at a fixed stress is an important parameter for experimental correlation purposes. A 30 day test period is considered sufficient to reveal failures in materials susceptible to sulfide stress cracking. In borderline cases, longer test periods may be desirable.

1.3 Safety Precautions: *Hydrogen sulfide is an extremely toxic gas which must be handled with care.* See discussion in Appendix 1 for safety considerations and toxicity of this gas.

Section 2: Reagents

2.1 Reagent Purity.

2.1.1 The gases, sodium chloride, acetic acid, and solvents shall be reagent or chemically pure (99.5% minimum purity) grade chemicals.

2.1.2 The water shall be distilled or deionized, tap water shall not be used (Appendix 2).

2.2 Preparation of Solution

2.2.1 Fifty grams of sodium chloride and 5 grams of glacial acetic acid (4.8 ml) are dissolved in 945 grams of water. The initial pH should be approximately 3. During the test, the pH may increase but not exceed 4.5.

Section 3: Test Specimens

3.1 The selection of the test specimens that can be used is often restricted by the size and shape of the material available for testing and by technical considerations of stress analysis, etc. The orientation of the specimen can affect the results and should be noted.

3.2 Tension Specimen (Figure 1)

3.2.1 The gage section of the tension specimen shall be 0.250 inch (6.4 mm) in diameter and 1 inch (25.4 mm) long (ASTM A-370). A subsize specimen with gage of 0.100 inch (2.54 mm) in diameter by 1 inch (25.4 mm) long is acceptable.

3.2.2 The radius of curvature to the large diameter portion shall be at least 0.25 inch (6.4 mm) to minimize stress concentrations.

3.2.3 Ends of the specimen must be long enough to accommodate seals for the test container and to make connections to the stressing fixture.

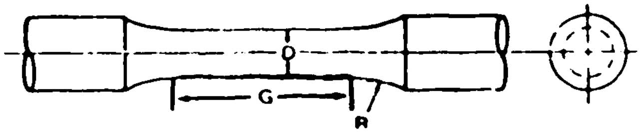
3.2.4 Machining of the specimens must be done carefully to avoid overheating and cold working in the gage section. The final two passes should remove about 0.002 inch (0.05 mm) metal total.

3.2.5 The specimen is finished to a surface roughness of 32 microinch (0.81 μm) or better.

3.3 Cleaning of Specimens

3.3.1 The specimen should be degreased with tetrachloroethylene or a similar solvent, rinsed with acetone and stored in a desiccator until ready for use.

3.3.2 Specimens must be handled only with clean tongs, polyethylene or cotton gloves after cleaning. Under no circumstances are the cleaned specimens to be handled with bare hands.



Dimension	D	G	R (min)
Standard	0.250 ± 0.005 inch (6.4 ± 0.13 mm)	1.00 inch (25.4 mm)	0.25 inch (6.4 mm)
Subsize	0.100 ± 0.002 inch (2.54 ± .005 mm)	1.00 inch (25.4 mm)	0.25 inch (6.4 mm)

FIGURE 1 Dimensions of the tension specimen.

Section 4: Test Equipment

4.1 Many types of stress jigs and test containers used for stress corrosion testing are acceptable for sulfide stress cracking testing. Consequently, the discussion in this section is intended to emphasize the required characteristics of the euipment to permit selection of suitable items and procedures.

4.2 Tension tests should be performed with constant load or sustained load devices.

4.3 Testing with constant or sustained load devices insures that susceptible materials will fail completely, eliminating the chance that a small crack will be overlooked in visual and microscopic examination of the test specimens.

4.4 Dead weight testers or hydraulic equipment, capable of maintaining constant pressure on a hydraulic cell, can be used for constant load testing.

4.5 Sustained load tests can be conducted with spring type devices and proving rings where relaxation in the fixtures or specimen will result in only a small percentage decrease in the applied load.

4.6 Because the test container will probably jacket the gage section of the specimen and possibly some of the thicker portion but not the stressing fixture itself, the specimen must be electrically isolated from any other metals in contact with the test solution.

4.6.1 The seals around the specimen must be electrically insulating and air tight but allow movement of the specimen with negligible friction.

4.6.2 In cases where it is feasible to immerse the complete test fixture in the test solution, the specimen must be electrically isolated from the stressing fixture with the fixture made of a material that is not susceptible to SSC. A susceptible fixture must be coated completely with a nonconducting impermeable coating.

4.7 Test Vessels

4.7.1 The size, shape, and entry ports of the test vessel will be determined by the actual test fixtures used to stress the specimens.

4.7.2 Vessels shall be capable of being purged to remove oxygen before the test is begun and also capable of keeping air out during the test. The use of a small outlet trap on the hydrogen sulfide effluent line to maintain 1 inch (2.54 cm) of water back pressure on the test vessel will prevent oxygen entry through small leaks or by diffusion up the vent line (Appendix 2, Reasons for Exclusion of Oxygen).

4.7.3 The test vessel shall be of a size that the solution volume can be maintained between 20 and 100 ml per square centimeter of specimen to standardize the drift of pH with time due to the consumption of the acetic acid.

4.7.4 The fixture, cell, etc. shall be essentially inert.

4.8 Temperature Control

4.8.1 The test solution shall be maintained at 75 ± 5 F (24 ± 2.8 C).

Section 5: Material Properties

5.1 Tensile testing shall be used for determining base material properties. Two or more specimens shall be pulled and averaged to determine the yield and ultimate strengths, percent elongation, and reduction of area for the material. It is desirable to machine a standard tension test specimen and the tension type stress corrosion test specimen from adjacent lengths of the item to be tested so that any minor variations in properties which normally occur from bar to bar can be minimized.

5.2 Some uncertainty still exists as to the fundamental material properties which correlate to the susceptibility

TABLE 1 – Suggested Data Reporting Forms for SSC Testing
(Artificial Data for Example Purposes Only)

Table A – Alloy Data

Alloy	C	Mn	S	P	Mo	Cr	Ni	Si	Heat Treatment	YS	TS	HRC
	Chemical Composition											
N-80-A	0.46	1.00	0.036	0.020	0.020				Q.T 1200 F (649 C)	120	130	27
N-80-B			Same						Q.T 1000 F (538 C)	134	147	32
N-80-C	0.42	1.13	0.028	0.020	0.018				N 1600 F (871 C), T 800 F (427 C)	94	122	24
4340-A	0.43	0.77	0.01	0.020	0.26	0.81	1.21		Q.T 1200 F (649 C)	116	127	27
9Cr-A	0.15	0.83	0.01	0.016	0.96	8.1			N 1700 F (927 C), T 1000 F (538 C)	120	152	36

Note. Q = Quenched, T = Tempered, YS = Yield Strength, and TS = Tensile Strength

Table B – Test Results

Time to Failure, Hours

Applied Stress, 100 psi (6.89 MPa)

Alloy	YS	40	60	75	80	85	90	95	100	120
N-80-A	120	NF	NF	NF	200	72			15	3
N-80-B	134	13	1.9		0.7				0.4	0.3
N-80-C	94	NF	NF		NF		NF	NF	62	15
4340-A	116	NF	NF	NF	F				F	F
9Cr-A	120	NF			F				F	F

Note. NF = No Failure, F = Failure During Test (32 days), and No Test

SSC. Consequently, all pertinent data on chemical composition, mechanical properties, heat treatment, and mechanical (such as percent cold reduction or prestrain) histories shall be determined and reported (Table 1) in addition to the tensile test data. It is emphasized that each different heat treatment, microstructure, etc., of a metal of fixed chemical composition shall be tested as though it were a different metal.

5.3 Before testing, hardness measurements shall be taken on the thick portion of each specimen.

Section 6: Test Procedures

6.1 Specimen Loading and Test Initiation

6.1.1 A variety of fixtures can be used to stress the specimens if the fixtures have the following important features:

6.1.1.1 Electrical isolation of [illegible] specimen from the fixture.

6.1.1.2 Ease of making precision load measurements.

6.1.1.3 Stable load behavior.

6.1.1.4 Proper environmental control.

6.1.2 Testing Sequence

6.1.2.1 A clean specimen is placed in the test cell and the necessary seals made.

6.1.2.2 The stressing fixture is placed in the test container, and then the test cell is purged with inert gas.

6.1.2.3 After the cell is purged, the load is applied carefully not to exceed the desired level of loading.

6.1.2.4 The test cell is filled immediately with deaerated solution and then saturated with hydrogen sulfide at a moderate flow rate (100 to 200 ml per minute) for 10 to 15 minutes.

6.1.2.5 It is necessary to maintain a continuous flow of hydrogen sulfide through the test container and outlet trap for the duration of the test at a low flow rate (a few bubbles per minute). This maintains the hydrogen sulfide concentration and a slight positive pressure to prevent air from entering the test container through small leaks.

6.1.2.6 With some highly alloyed corrosion resistant materials, it may be necessary to follow an alternate loading sequence such as 6.1.2.1, 6.1.2.4, 6.1.2.3 to prevent reformation of a protective film. (If used, this alternate sequence shall be reported.)

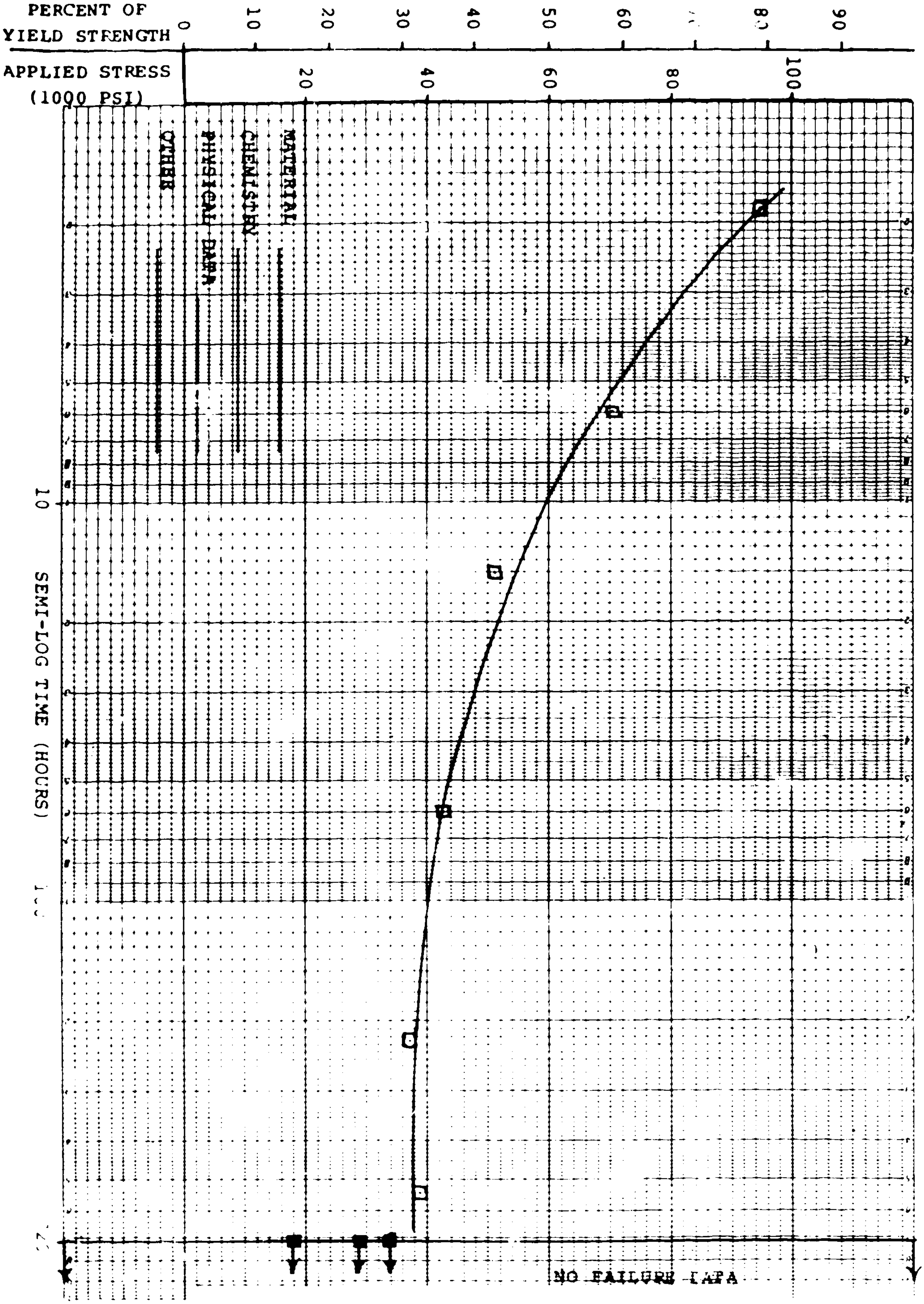


FIGURE 2 Presentation of data by semilog graph

6.2 Failure Detection

6.2.1 Time-to-failure shall be recorded using electrical timers and microswitches

6.2.2 Tension specimens may be stressed at convenient increments of the yield strength

6.2.3 Additional specimens shall be tested to closely define the fail/no fail stress

Section 7: Reporting of Test Results

7.1 Time-to-failure and no failure data are reported for each stress level.

7.2 Table 1 shows a suggested format for reporting the data. Presentation of the data may also be shown on semilog graph paper (Figure 2).

7.3 All chemical compositions, heat treatment, physical property, and other data taken shall be reported.

Appendix 1

Safety Considerations in Handling Hydrogen Sulfide

Toxicity

Hydrogen sulfide is perhaps responsible for more industrial poisoning accidents than any other single chemical. A number of these accidents have been fatal. Hydrogen sulfide shall be handled with caution and any experiments using it planned carefully. The maximum allowable OSHA[1] concentration in the air for an 8 hour work day is 20 parts per million (ppm), well above the level detectable by smell. However, the olfactory nerves can become deadened to the odor after exposure of 2 to 15 [illegible], dependent on concentration, so that odor is [illegible] completely reliable alarm system.

Briefly, the following are some of the human physiological reactions to various concentrations of hydrogen sulfide. Exposure to concentrations in the range of 150 to 200 ppm for prolonged periods may cause edema of the lungs. Nausea, stomach distress, belching, coughing, headache, dizziness, and blistering are signs and symptoms of poisoning in this range of concentration. Pulmonary complications, such as pneumonia, are strong possibilities from such subacute exposure. At 500 ppm, unconsciousness usually results within 30 minutes and results [illegible] acute toxic reactions. In the 700 to 1000 ppm range, unconsciousness may occur in less than 15 minutes and death occur within 30 minutes. At concentrations above 1000 ppm, a single lungfull may result in instantaneous unconsciousness with death quickly following due to complete respiratory failure and cardiac arrest.

Additional information on the toxicity of hydrogen sulfide can be obtained from the *Chemical Safety Data Sheet SD-36*, adopted January 1950, available from the Manufacturing Chemists Association, 1825 Connecticut Ave., N.W., Washington, D.C. 20009, and from *Dangerous Properties of Industrial Materials* by N. Irving Sax, published in 1968 by Reinhold Book Corp., New York, New York. American Conference of Governmental Industries Hygenists [illegible]

Fire and Explosion Hazards

Hydrogen sulfide is a flammable gas, yielding poisonous sulfur dioxide as a combustion product. In addition, its explosive limits range from 4 to 46% in air. Appropriate precautions should be taken to prevent these hazards from developing.

Experimental Suggestions

All tests should be performed in a hood with adequate ventilation to exhaust all the H_2S. The H_2S flow rates should be kept low to minimize the quantity exhausted. A 10% caustic absorbent solution for effluent gas can be used to further minimize the quantity of H_2S gas exhausted. This solution will need periodic replenishment. Provision should be made to prevent backflow of the caustic solution into the test vessel if the H_2S flow is interrupted. Suitable safety equipment should be used when working with H_2S.

Particular attention should be given to the output pressure on the pressure regulators as the downstream pressure frequently will rise as corrosion product debris, etc., and interfere with regulation at low flow rates. Gas cylinders should be securely fastened to prevent tipping and breakage of the cylinder head. Because hydrogen sulfide is in liquid form in the cylinders, the high pressure gage should be checked frequently as relatively little time will elapse after the last liquid evaporates until the pressure drops from 2[illegible]0 psi (1.[illegible] MPa) to atmospheric pressure. The cylinder should be replaced by the time it reaches 75 to 100 psi (0.5 to 0.7 MPa) because the regulator control may become erratic. Flow should not be allowed to stop without closing a valve or disconnecting the tubing at the test vessel because the solution will continue to absorb H_2S and [illegible] upstream into the [illegible]line regulator and even the cylinder. A check valve in the line should prevent the problem if the valve works properly. However, if such an accident occurs, the remaining hydrogen sulfide should be vented as rapidly and [illegible] as possible and the manufacturer notified so that the cylinder can receive special attention.

Reference

1. OSHA Rules and Regulations (Federal Register, Vol. 37, No. 202, Part II, dated October 18, 1972).

Appendix 2

Explanatory Notes on Test Method

Reasons for Reagent Purity (Section 2)

Water impurities of major concern are alkaline or acid buffering constituents which would alter the pH of the test solution and organic and inorganic compounds which could change the nature of the corrosion reaction. Oxidizing agents could also convert part of the hydrogen sulfide to soluble products such as polysulfides and polythionic acids, which may also affect the corrosion process.

Alkaline materials (magnesium carbonate, sodium silica aluminate, etc.) are often added to (or not removed from) commercial grades of sodium chloride to assure free flowing characteristics and can greatly affect the pH.

Trace oxygen impurities in the purge gas would be much more critical if the nitrogen (or other inert gas) were to be continuously mixed with the hydrogen sulfide in order to obtain a [illegible] partial pressure of hydrogen sulfide in the gas and [illegible] a lower hydrogen sulfide concentration in solution. Oxidation products could accumulate resulting in changes in corrosion rate and/or hydrogen entry rate (Appendix 2, Reasons for Exclusion of Oxygen).

Preparation of Tensile Specimen (Section 3)

It should be emphasized that all machining operations should be performed carefully and slowly so that overheating, excessive gouging, and cold work, etc., do not alter critical physical properties of the material. Surface smoothness is critical in unnotched specimens.

Reasons for Exclusion of Oxygen

Obtaining and maintaining an environment with minimum dissolved oxygen contamination is considered very important because of significant effects noted in field and laboratory studies.

1. Oxygen contamination in brines containing H_2S can result in drastic increases in corrosion rates by as much as two orders of magnitude. Generally, the oxygen can also reduce hydrogen evolution and entry into the metal. Systematic studies of the parameters affecting these phenomena (as they apply to SSC) have not been reported in the literature.

2. Small amounts of oxygen or ammonium polysulfide are sometimes added to aqueous refinery streams in conjunction with careful pH control near 8 to minimize both corrosion and hydrogen blistering. The effectiveness is attributed to an alteration of the corrosion product.

In the absence of sufficient data to define and clarify the effects of these phenomena on SSC, it is thought that all reasonable precautions to exclude oxygen should be taken. The precautions stated in this Test Method will minimize the effects of oxygen with little increase in cost, difficulty, or complexity.

APPENDIX 2

MATERIAL REQUIREMENT

technical practices committee

NACE Standard MR-01-75
(1980 Revision)

Replaces original version and 1978 Revision of NACE Standard MR-01-75 and NACE Publication 1F166.

Material Requirement

Sulfide Stress Cracking Resistant Metallic Material for Oil Field Equipment

Approved March, 1975
Revised April 1978
Revised August 1979
National Association of Corrosion Engineers
1440 South Creek
Houston, Texas 77084
713/492 0535

The National Association of Corrosion Engineers issues this Standard in conformity to the best current technology regarding the specific subject. This Standard represents minimum requirements and should in no way be interpreted as a restriction on the use of better procedures or materials. Neither is this Standard intended to apply in all cases relating to the subject. Unpredictable circumstances may negate the usefulness of this Standard in specific instances.

Whenever possible the recommended materials are defined by reference to accepted Standards, such as AISI, API or ASTM Standards. However, some acceptable materials could n[illegible] precisely defined without designation by trade name [illegible] materials have been designated as acceptable on the assumption that their nominal chemical composition and physical properties will remain the same as those possessed at the time of this Standard.

The National Association of Corrosion Engineers assumes no responsibility for the interpretation or use of this Standard. The National Association of Corrosion Engineers makes no representation, warranty or guarantee in connection with publication of this Standard, and hereby expressly disclaims any liability or responsibility for loss or damage resulting from its use or for any violation of any federal, state, or municipal regulation or law with which this Standard might conflict.

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Foreword

This NACE Standard (Material Requirement) is another step in a series of committee stud[illegible] reports, symposia, and Standards which have [illegible] issued by Group Committee T-1 (Corrosion Cont[illegible]oleum Production) relating to the general probl[illegible]ulfide stress cracking (SSC) of metals. Much of this work has been directed toward oil and gas production service. Many of the guidelines and specific requirements in this Standard are based on field experience with these materials in specific components and may [illegible] applicable to other components and equipment in the [illegible] production industry or to other industries. The user of this Standard must be cautious in extrapolating the content of this standard or broader usage than covered by this Standard.

The materials, heat treatments, and metal property requirements given in this Standard represent the best judgement of Task Groups T-1F-1, T-1F-16, and T-1F-18 and their sponsoring Unit Committee, T-1F, Metallurgy of Oil Field Equipment.

This NACE Standard updates MR-01-75, 1975 edition, entitled "Materials for Valves for Resistance to Sulfide Stress Cracking in Production and Pipeline Service," which replaced NACE Publication 1F166 (1973 revision) entitled "Sulfide Cracking Resistant Metallic Materials for Valves for Production and Pipeline Service" and also NACE Publication 1B163 entitled "Recommendations of Materials for Sour Service" (which included Tentative Specifications 150 on valves, 51 on severe weight loss, 60 on tubular goods, 50 on nominal weight loss).

Revision of this Standard will be considered to reflect changes in technology. See Paragraph 1.6.

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8.[illegible] S[illegible] R[illegible]

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Section 1: General

1.1 Coverage This Standard covers metallic material requirements for resistance to sulfide stress cracking (SSC) for petroleum production, drilling, gathering and flowline equipment, and field processing facilities to be used in H_2S bearing hydrocarbon service. This Standard is applicable to the materials used for equipment covered by API,(1) ANSI,(2) ASTM,(3) ASME,(4) and CSA(5) Standards (or by equivalent standards or specifications of other countries). This Standard does not include and is not intended to include design specifications. Other forms of corrosion or other modes of failure, although outside the scope of this Standard, should also be considered in design and operation of equipment. Severe corrosive conditions may lead to failures by mechanisms other than sulfide stress cracking and should be mitigated by corrosion inhibition or materials selection guidelines outside the scope of this document. For example, some lower strength steels used for pipelines and vessels may be subjected to failure by "blister cracking" or "step wise cracking" due to hydrogen damage associated with general corrosion in the presence of hydrogen sulfide.(6)

1.2 Applicability This Standard is applicable to all components of equipment exposed to sour environments, as defined in Paragraph 1.3, failure of which by SSC would (1) prevent the equipment from being restored to an operating condition while continuing to contain pressure, (2) compromise the integrity of the pressure containment system, and (3) prevent the basic function of the equipment. Materials selection for items such as atmospheric and low pressure systems (see Paragraph 1.3), water handling facilities, sucker rods, and subsurface pumps are covered by other API and NACE Standards and not by this Standard.

1.3 Sour Environment Fluids containing water as a liquid and hydrogen sulfide are sour environments and may cause sulfide stress cracking (SSC) of susceptible materials. This phenomenon is affected by complex interaction of parameters including (1) metal chemical composition, strength, heat treatment, and microstructure, (2) pH, (3) hydrogen sulfide concentration and total pressure, (4) total tensile stress, (5) temperature, and (6) time. The user shall determine the environmental conditions in which the metallic materials are to meet the requirements of this Standard. The following guidelines are offered to assist the user in making this judgement.

1.3.1 Sour Gas Material shall be selected to be resistant to SSC or the environment should be controlled if the gas being handled is at a total pressure of 65 psia or greater and if the partial pressure of H_2S in the gas is greater than 0.05 psia. Systems operating below 65 psia total pressure or below 0.05 H_2S partial pressure are outside the scope of this Standard. Partial pressure is determined by multiplying the mol fraction (mol % ÷ 100) of H_2S in the gas times the total system pressure. Figure 1 provides a convenient means of determining whether the partial pressure of H_2S in a sour environment exceeds 0.05 psia. Examples: (1) Partial pressure of H_2S in a system containing 0.01 mol % H_2S (100 ppm or 6.7 grains per 100 SCF) at a total pressure of 1000 psia exceeds 0.05 psia (Point "A" on Figure 1), and (2) partial pressure of H_2S in a system containing 0.005 mol % H_2S (50 ppm or 3.3 grains per 100 SCF) at a total pressure of 200 psia does not exceed 0.05 psia (Point "B" on Figure 1).

1.3.2 Sour Oil and Multiphases Sour crude oil systems which have operated satisfactorily using off-the-shelf equipment are outside the scope of this Standard when the fluids being handled are either crude oil, or two or three phase crude, water and gas when (1) the maximum gas/liquid ratio is 5000 SCF/Bbl, (2) the gas phase contains a maximum of 15% H_2S, (3) the partial pressure of H_2S in the gas phase is a maximum of 10 psia, and (4) the surface operating pressure is a maximum of 265 psia (see Figure 2). The satisfactory service of off-the-shelf equipment in these low pressure systems is believed to be a result of the inhibitive effect of the oil and the low stresses encountered under the low pressure conditions.

1.4 Control of Sulfide Stress Cracking SSC may be controlled by any or all of the following: (1) The use of metallic materials and processes described in this Standard, (2) controlling the environment, and/or (3) isolating the components from the sour environment. During drilling and workover operations, metals susceptible to SSC have been used successfully by controlling drilling fluid properties.

1.5 Acceptable Materials The acceptable metallic materials and manufacturing processes listed in Sections 3 through 11 and Tables 1 through [illegible] have satisfactory sulfide stress cracking service in sour environments when (1) manufactured to the heat treatment and mechanical properties specified and (2) used under the specific conditions noted.

1.6 Procedures for the Addition of New Materials or Processes The guidelines and specific requirements in this Standard are based on satisfactory field experience. Additional materials will be added to those listed whenever

---

(1) American Petroleum Institute, 300 Corrigan Tower, Dallas, Texas, 75201

(2) American National Standards Institute, 1403 Broadway, New York, New York, 10018

(3) American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania, 19103

(4) American Society of Mechanical Engineers, 345 East 47th Street, New York, New York, 10017

(5) Canadian Standards Association, 178 Rexdale Blvd., Rexdale, Ontario, Canada

(6) E. M. Moore and J. J. Warga, "Factors Influencing the Hydrogen Cracking Sensitivity of Pipeline Steels," Paper Number 144, Corrosion/76, March, 1976

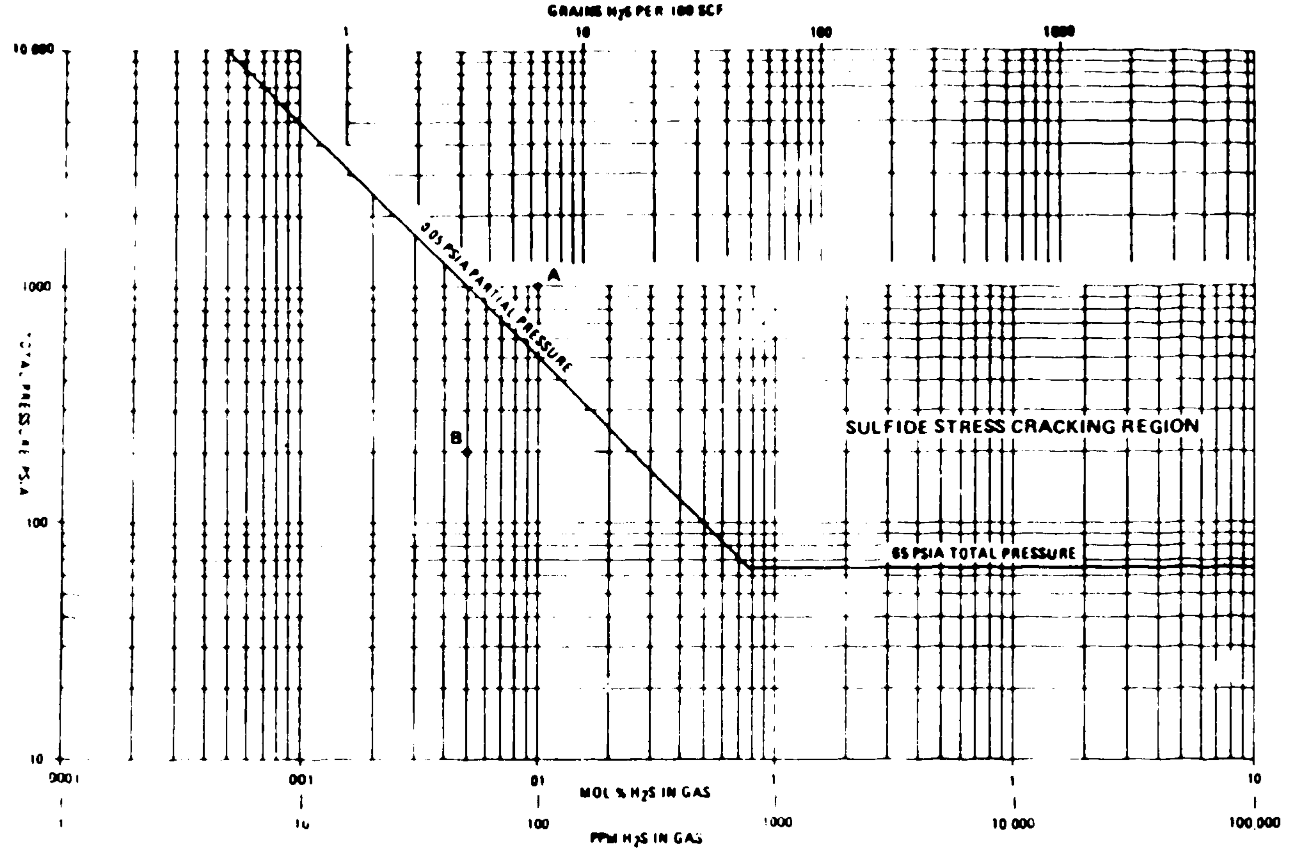

FIGURE 1 - Sour gas systems (see Paragraph 1.3.1)

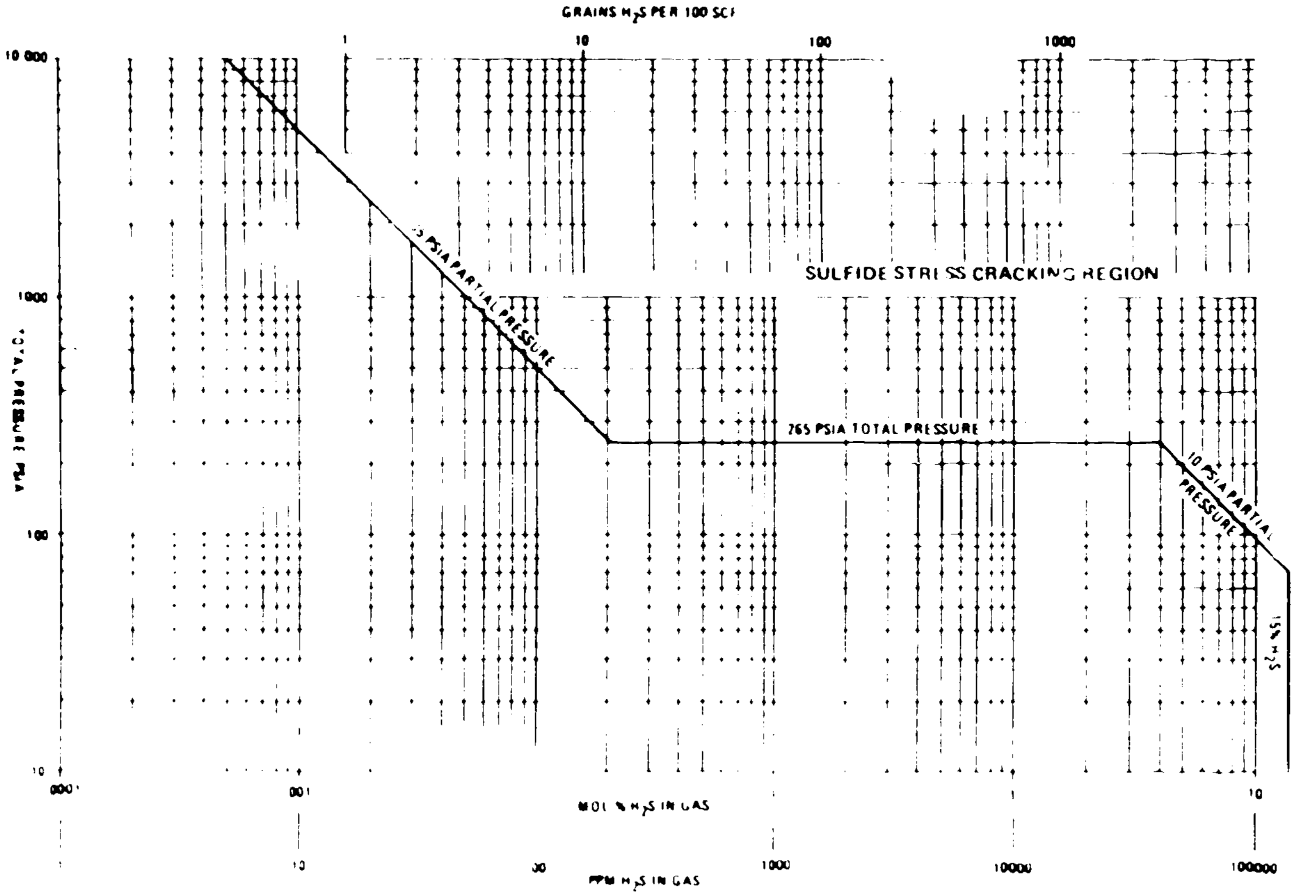

FIGURE 2 - Sour multiphase systems (see Paragraph 1.3.2)

a manufacturer or user establishes to the satisfaction of NACE that such materials are acceptable. Requests for revision of the Standard should be made in writing to NACE Headquarters as described in the NACE Standards Manual. These requests should propose the specific changes desired and be supported by appropriate documentation which shall include a complete description of the materials or processes and laboratory or field test data, service performance, or other technical justification. The requested change shall be reviewed and balloted as described in the NACE Standards Manual. Laboratory data, provided in accordance with NACE Test Method TM-01-77, is one accepted method for providing this required laboratory test information.

1.7 Hardness Requirements

1.7.1 The correlation between SSC, heat treatment, and hardness has been reliably documented by extensive laboratory and field service data. Since hardness testing is nondestructive, it is widely used by manufacturers as a quality control method and by users as a field inspection method. Accurate hardness testing requires strict compliance with the methods described in appropriate ASTM Standards.

1.7.2 Sufficient hardness tests should be made to establish the actual hardness of the material or component being examined. Hardness measurements exceeding the value permitted by this document can be considered acceptable if the average of several readings taken within close proximity does not violate the value permitted by the document and no individual reading is greater than 2 HRC units above the acceptable value. The number and location of test area is outside the scope of this standard.

1.7.3 **Rockwell "C" Hardness Scale (HRC) is referred to throughout this standard. Hardness values measured by the Rockwell "C" scale shall be the primary basis for acceptance.** However, when warranted, Brinell (HBN) or other hardness scales may be used. Microhardness acceptance criteria are considered outside the scope of this document because insufficient data were available to provide a correlation between microhardness values and SSC resistance. When applicable, hardness conversions shall be made in accordance with the appropriate table in the latest editions of ASTM E140 Standard Hardness Conversion Table for Metals or Federal Standard No. 151, Method 241.1[7] Hardness Conversion Table for Steel.

1.8 Materials Handling. Although this Standard concerns materials intended for sulfide service, this Standard is not to be construed to mean that products conforming to these requirements will be resistant to SSC by sulfide-containing sour environments under all conditions. Improper design, manufacturing, installation, or handling can cause resistant materials to become susceptible to SSC.

1.9 Procurement. It is the responsibility of the user to determine the expected operating conditions and to specify when this Standard applies. This Standard includes a variety of materials which might be used for any given component. The user may select specific materials for use on the basis of operating conditions which include pressure, temperature, corrosiveness, fluid properties, etc. For example, in selecting bolting components, the pressure rating could be affected. The following could be specified at the user's option: (1) materials used from this Standard by the manufacturer, and (2) materials from this Standard proposed by the manufacturer and approved by the user.

Section 2 Definitions

Age Hardening: Hardening by aging, usually after rapid cooling or cold working.

Aging: A change in metallurgical properties that generally occurs slowly at room temperature (natural aging) and more rapidly at higher temperatures (artificial aging).

Annealing: Heating to and holding at a suitable temperature and then cooling at a suitable rate, for such purposes as reducing hardness, improving machinability or obtaining desired properties.

Austenite: A solid solution of carbon and/or other elements in face-centered cubic iron.

Austenitic Steel: An alloy steel whose microstructure at room temperature normally consists of austenite.

Austenitizing: Forming austenite by heating a ferrous alloy into the transformation range (partial austenitizing) or above the transformation range (complete austenitizing).

Autofrettage: A technique whereby residual compressive stresses are created at the interior of a thick walled component following application and release of internal pressure which causes yielding of the metal near the ID or bore of the component.

Blowout Preventers (BOP): Mechanical devices capable of containing pressure, used for control of well fluids and drilling fluids during drilling operations.

Brazing: Joining metals by flowing a thin layer of capillary thickness of a lower melting point nonferrous filler metal in the space between them.

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[7] Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402

Burnishing Smoothing surfaces through frictional contact between the work and some hard pieces of material such as hardened steel balls

Carbon Steel An alloy of carbon and iron containing carbon up to about 2% and manganese up to about 1 65%, containing residual quantities of other elements except those intentionally added for deoxidation (usually silicon and/or aluminum) Carbon steels used in the petroleum industry usually contain less than approximately 0 8% carbon

Case Hardening Hardening a ferrous alloy so that the outer portion, or case, is made substantially harder than the inner portion, or core Typical processes are carburizing, cyaniding, carbonitriding, nitriding, induction hardening, and flame hardening

Cast (Casting) Metal that is obtained at or near its finished shape by the solidification of molten metal in a mold

Cast Iron An iron and carbon alloy containing approximately 2 to 4% carbon Cast irons may be classified as (1) Gray cast iron cast iron that gives a gray fracture due to the presence of flake graphite, (2) white cast iron cast iron that gives a white fracture due to the presence of cementite (Fe_3C), (3) malleable cast iron white cast iron that is thermally treated to convert most or all of the cementite to graphite (temper carbon), (4) ductile (nodular) cast iron cast iron that has been treated while molten with an element (usually magnesium or cerium) that converts the graphite to a spheroidal form, and (5) austenitic cast iron cast iron with sufficient nickel added to produce an austenitic structure

Chloride Stress Corrosion Cracking Failure by cracking under the combined action of tensile stress and corrosion in the presence of chlorides and water

Cold Deforming See Cold Working

Cold Forming See Cold Working

Cold Reducing See Cold Working

Cold Working Deforming metal plastically at a temperature lower than its recrystallization temperature

Double Tempering A treatment in which normalized or quench hardened steel is given two complete tempering cycles (cooling to room temperature after each cycle) at the same or substantially the same temperature with the object of tempering any martensite which may have formed during the first tempering cycle

Duplex (Austenitic Ferritic) Stainless Steel A stainless steel whose microstructure at room temperature consists of austenite and ferrite

Ferrite: A solid solution of carbon and/or other elements in body-centered cubic iron.

Ferritic Steel A steel whose microstructure at room temperature normally consists of ferrite.

Ferrous Metal: A metal in which the major constituent is iron

Free Machining Steel: Steel to which elements such as sulfur, selenium, and lead have been intentionally added to improve machinability

Hardness: Resistance of metal to plastic deformation, usually by indention

Heat Treatment: Heating and cooling a solid metal or alloy in such a way as to obtain desired properties Heating for the sole purpose of hot working is excluded from this definition

Heat Affected Zone (HAZ): That portion of the base metal that was not melted during brazing, cutting, or welding, but whose microstructure and properties were altered by the heat of welding, brazing, or cutting.

Hot Rolling Hot working a metal through dies or rolls to obtain a desired shape.

Hot Working: Deforming metal plastically at a temperature above the recrystallization temperature.

Low Alloy Steel: Steel containing less than about 5% total alloying elements, but more than specified for carbon steel

Lower Critical Temperatures: The temperatures at which austenite begins to form during heating or at which the transformation of austenite is completed during cooling

Manufacturer: The firms or persons involved in some or all phases of manufacturing or assembly of components For example the firm used to upset tubing is considered a manufacturer

Martensite A supersaturated solid solution of carbon in iron characterized by an acicular (needle-like) microstructure

Martensitic Steel A steel in which a microstructure of martensite can be secured by quenching at a cooling rate fast enough to avoid the formation of other microstructures

Microstructure The structure of a metal as revealed by microscopic examination of a suitably prepared specimen

Nonferrous Metal A metal in which the major constituent is not iron

Normalizing: Heating a ferrous alloy to a suitable temperature above the transformation range (austenitizing), holding at temperature for a suitable time, and then cooling in still air to a temperature substantially below the transformation range.

Partial Pressure: In a mixture of gases, each component exerts the pressure which it would exert if present alone at the same temperature in the total volume occupied by the mixture. The partial pressure of each component is equal to the total pressure multiplied by its mol fraction in the mixture. For most gases, the mol fraction is equal to the volume fraction of the component.

Plastic Deformation: Deformation that does or will remain permanent after removal of the stress that caused it.

Precipitation Hardening: Hardening caused by the precipitation of a constituent from a supersaturated solid solution.

Quench Hardening: Hardening a ferrous alloy by austenitizing and then cooling rapidly enough so that some or all of the austenite transforms to martensite.

Quench and Temper: Quench hardening followed by tempering.

Recrystallization Temperature: The approximate minimum temperature at which a new strain-free structure is produced in cold worked metal within a specified time.

Residual Stress: Stress present in a component that is free of external forces or thermal gradients.

Rockwell "C" Hardness (HRC): A hardness value obtained by use of a cone shaped diamond indentor and a load of 150 kilograms. Rockwell hardness conversions may be made in accordance with the appropriate tables in ASTM E140 or Federal Standard No. 151 Method 241.1.(7)

Slush Pump: Pump normally used to circulate drilling fluids through the drill stem into the annulus of the hole for the purpose of removing cuttings and maintaining a hydrostatic head.

Solid Solution: A single solid homogenous crystalline phase containing two or more chemical species.

Solution Heat Treatment: Heating a metal to a suitable temperature and holding at that temperature long enough for one or more constituents to enter into solid solution, then cooling rapidly enough to retain the constituents in solution.

Sour Environment: See Paragraph 1.3.

Stainless Steel: Steel containing sufficient chromium (usually more than approximately 11%) to render the steel corrosion resistant. Other elements may be added to secure special properties.

Stress Relieving: Heating a metal to a suitable temperature below the transformation range (AC_1), holding at temperature long enough to reduce residual stresses, and then cooling slowly enough to minimize the development of new residual stresses.

Sulfide Stress Cracking (SSC): Brittle failure by cracking under the combined action of tensile stress and corrosion in the presence of water and hydrogen sulfide. See Paragraph 1.1 for blistering.

Surface Hardening: See Case Hardening.

Tempering: Reheating a normalized or quench hardened ferrous alloy to a temperature below the transformation range (AC_1), holding at temperature for a suitable time, and then cooling at any rate desired.

Tensile Strength: In tensile testing, the ratio of maximum load to original cross-sectional area. Also called "ultimate strength".

Tensile Stress: The net tensile component of all combined stresses, axial or longitudinal, circumferential or "hoop", and residual.

Transformation Ranges: Those ranges of temperature for steels within which austenite forms during heating and transforms during cooling. The two ranges are distinct, sometimes overlapping, but never coinciding.

Tubular Component: A cylindrical component having a longitudinal hole that is used in drilling production operations for conveying fluids (pipe).

Welding: Joining two or more pieces of metal by applying heat, pressure, or both with or without filler metal, to produce a localized union through fusion or recrystallization across the interface.

Weldment: An assembly whose components are joined by welding. A weldment includes both the weld metal and the heat affected zone (HAZ).

Weld Metal: That portion of a weldment which has been molten during welding.

Wrought: Metal in the solid condition that is formed to a desired shape by working (rolling, extruding, forging, etc.) usually at an elevated temperature.

Yield Strength: The stress at which a material exhibits a specified deviation from the proportionality of stress to strain. The deviation is expressed in terms of strain by either: (1) the offset method (usually at a strain of 0.2%) or (2) the total-extension-under-load method (usually at a strain of 0.[illegible]).

Section 3: Ferrous Metals

Metallic materials shall meet the requirements of this section if they are to be exposed to sour environments (See Paragraph 1.3).

3.1 Most ferrous metals, hardenable by heat treatment and/or cold work, can be made susceptible to SSC. Conversely, many ferrous metals can be heat treated to provide acceptable resistance to SSC. The following paragraphs describe heat treatments for specific materials which will provide acceptable resistance to SSC (refer to Section 5 for methods to minimize the effects from fabrication).

3.2 The materials listed in Tables 1 and 2 are acceptable for use in sour environments in conditions noted in Paragraphs 3.3, 3.5, 3.6, 3.7, and 3.8.

3.3 Carbon and Low Alloy Steels

3.3.1 Carbon and low alloy steels are acceptable at HRC 22 maximum in the following heat treatment conditions provided they contain less than 1% Ni and meet the criteria of Paragraph 3.3.2, 3.9.1, and Section 5: (1) hot rolled (carbon steels only), (2) annealed, (3) normalized, (4) normalized and tempered, (5) normalized, austenitized, quenched and tempered, and (6) quenched and tempered. A partial listing of acceptable API, ASTM, and AISI(8) carbon and low alloy steels is presented in Table 1. Materials listed in Table 4 are acceptable under the environmental conditions noted.

3.3.2 Subsequent to any cold deformation by rolling, cold forging, or other manufacturing processes resulting in a permanent, extreme fiber deformation greater than 5%, the component shall be thermally treated (stress relieved) in accordance with Section VIII, Division 1 of the ASME Code, except that the minimum temperature shall be 595 C (1100 F). The component shall have a maximum hardness of HRC 22 after such thermal treatment.

This requirement does not apply to pipe grades listed in Table 4 or to cold work imparted by pressure testing required per applicable code. Cold rotary straightening of pipe is acceptable.

Cold worked line pipe connections of A-53 Grade B, A-106 Grade B, and API 5LX-42 or lower strength grades of these specifications are acceptable with up to 15% strain provided the hardness of the strained area does not exceed 190 HB.

3.3.3 Low alloy steels in the Cr, Mo class (AISI 41XX and its modifications) are acceptable as tubulars and tubular components at a maximum hardness of HRC 26 in the quenched and tempered condition.

Careful attention to chemical composition and heat treatment is required to ensure SSC resistance of these alloys at hardness levels greater than HRC 22. Accordingly, it is common practice for the user when using this alloy at hardness above HRC 22 to conduct SSC tests (See Paragraph 1.6) to determine that the material is equivalent in SSC performance to similar materials which have given satisfactory service in sour environments.

If cold straightened after heat treatment, the minimum stress relief temperature following straightening shall be 480 C (900 F). If hot straightened, the minimum straightening temperature shall be 510 C (950 F).

3.4 Cast Iron

3.4.1 Gray, austenitic, and white cast irons are not acceptable because of low ductility for use as a pressure containing member in equipment covered by API and other appropriate Standards. Cast iron and austenitic ductile iron shall not be used in nonpressure containing internal parts related to these API Standards without approval of the purchaser.

3.4.2 Ferritic ductile iron, Grade ASTM A-395, is acceptable for equipment when its use is acceptable under API, ANSI, and other industry Standards.

3.5 Austenitic Stainless Steels(9)

3.5.1 Austenitic stainless steel with chemical composition as specified in accordance with the standards listed in Table 2, either cast or wrought, are acceptable at a hardness of HRC 22 maximum in the annealed condition, provided they are free of cold work designed to enhance their mechanical properties.

3.6 Ferritic Stainless Steels

3.6.1 Ferritic stainless steels, listed in Table 2, are acceptable at hardness levels of HRC 22 maximum in the annealed condition, provided they meet the criteria of Section 5.

3.7 Martensitic Stainless Steels(10)

3.7.1 Martensitic stainless steels, listed in Table 2, are acceptable at hardness levels of HRC 22 maximum in the wrought or cast condition, provided they are normalized or austenized and quenched, followed by double tempering and provided they meet the criteria of Section 5. Both tempering temperatures shall be 620

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(8) American Iron and Steel Institute, 1000 16th Street North West, Washington, D.C., 20036

(9) These materials may be subject to chloride stress corrosion cracking in certain environments

(10) Valve manufacturers generally do not use these materials for valve stems or other highly stressed components used in sour service

C (1150 F) minimum and the second tempering temperature shall be lower than the first tempering temperature

3.7.2 Subsequent to cold deformation (See Paragraph 3.3.2), the part shall be furnace stress relieved at 620 C (1150 F) minimum to a maximum hardness of HRC 22

3.8 Precipitation Hardening Stainless Steels(9)

3.8.1 Wrought 17Cr-4Ni precipitation hardening steels, listed in Table 2, are acceptable at hardness levels of HRC 33 maximum in the special heat treatment conditions listed in Appendix A.

3.8.2 Precipitation hardening austenitic stainless steels, with chemical composition as specified in accordance with ASTM A-453 Grade 660 or ASTM A-638 Grade 660 (A-286), listed in Table 2, are acceptable at hardness levels of HRC 35 maximum in the solution annealed and aged condition or double aged condition.

3.8.3 Snap rings processed from PH 15-7 Mo in the H950 solution annealed and aged condition and heat treated in accordance with Appendix C are acceptable at HRC 30-32.

3.9 Free-Machining Steels

3.9.1 Free-machining steels shall not be used under conditions described in Paragraph 1.2.

3.10 Duplex (Austenitic/Ferritic) Stainless Steels

3.10.1 Duplex stainless steels, listed in Table 2, are acceptable to a maximum hardness of HRC 28 in the solution annealed condition. (Reference footnote 9).

Section 4: Nonferrous Metals(11)-(14)

Metallic materials shall meet the requirements of this section if they are to be exposed to sour environments (See Paragraph 1.3).

4.1 Alloys listed in this section and Table 3 are acceptable in the conditions noted under each metal at a maximum hardness of HRC 35.

4.1.1 Nickel Copper Alloys

4.1.1.1 Nickel-copper alloys (such as Monel 400)

4.1.1.2 Nickel-copper-aluminum alloys (such as Monel K-500) in the hot rolled and age hardened, solution annealed, or solution annealed and age hardened condition.

4.1.2 Nickel-Iron-Chromium Alloys

4.1.2.1 Nickel-iron-chromium alloys (such as Incoloy 800)

4.1.2.2 Nickel-iron-chromium-molybdenum alloys (such as Incoloy 825)

4.1.3 Nickel-Chromium Alloys

4.1.3.1 Nickel-chromium alloys (such as Inconel 600).

4.1.3.2 Nickel-chromium-aluminum alloys (such as Inconel X-750) in the solution annealed and aged, solution annealed, hot rolled, or hot rolled and aged conditions.

4.1.4 Nickel-Chromium-Molybdenum Alloys

4.1.4.1 Nickel-chromium-molybdenum-aluminum alloys (such as Inconel 625, Hastelloy C, Hastelloy G, and Hastelloy X).

4.1.4.2 Nickel-chromium-molybdenum-aluminum alloys (such as Inconel 718) in the solution annealed and aged, solution annealed, hot rolled, or hot rolled and aged conditions.

4.1.5 Cobalt-Nickel-Chromium-Molybdenum Alloys (such as MP35N, Elgiloy, Havar, and Nimonic 105)

4.1.6 Cobalt-Nickel-Chromium-Tungsten Alloys (such as Cyclops L605 and Haynes Alloy No. 25) are acceptable.

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(11) See Appendix B.

(12) These materials may be subject to stress corrosion cracking failure when highly stressed and exposed to sour environments or some well stimulating acids either with or without inhibitors.

(13) Some of the materials in the wrought condition may be susceptible to failure by hydrogen embrittlement when strengthened by cold work and stressed in the transverse direction.

(14) Plastic deformation in service may increase the SSC susceptibility of these alloys.

4.2 Coatings, Overlays, and Castings

Materials listed in this section and Table 3 are acceptable.

4.2.1 Cobalt-Chromium-Tungsten Alloys (such as Stellites) are acceptable in the "as cast" condition.

4.2.2 Nickel-Chromium-Boron Alloys (such as Colmonoys)

4.2.3 Tungsten Carbide Alloys (such as cast, cemented, or thermally sprayed powders)

4.2.4 Nickel-Boron Alloys (ASM 4779 such as Ancorspray)

4.2.5 Ceramics (such as cast or thermally sprayed powders)

4.3 Other Alloys

Materials listed in this section and Table 3 are acceptable.

4.3.1 Aluminum Base Alloys

4.3.2 Copper Alloys[15]

Section 5: Fabrication

Metallic materials shall meet the requirements of this section if they are to be exposed to sour environments (See Paragraph 1.3).

5.1 Overlays

5.1.1 Overlays applied to carbon and low alloy steels or to martensitic stainless steels by thermal processes such as welding, silver brazing, or spray metallizing systems are satisfactory for use in sour environments, provided the substrate does not exceed the lower critical temperature during application. In those cases where the lower critical temperatures are exceeded, the component must be heat treated or thermally stress relieved according to procedures which have been shown to return the base metal to a maximum hardness of HRC 22.

5.1.2 Carbides and ceramics are satisfactory, subject to the conditions of Paragraph 5.1.1 and Section 4.

5.1.3 Joining of dissimilar metals, such as cemented carbides to alloy steels by silver brazing, is acceptable. The base metal after brazing shall meet the requirements of Paragraph 5.1.1.

5.1.4 The materials listed in Tables 1-3 and Sections 3 and 4 are acceptable as weld overlays provided they meet the provisions of Paragraph 5.1.1.

5.2 Welding

5.2.1 Welding procedures[16] shall be used to produce weldments which comply with the requirements specified for the base metal in Sections 3 and 4. Welding procedure qualifications, per API, ASME, or other appropriate specifications, shall be run on any welding procedure which is to be used. Welders using this procedure shall be familiar with the procedure and shall be capable of making welds which comply with the procedure.

5.2.1.1 Tubular products listed in Table 4 with specified minimum yield strength of 52 ksi or less and pressure vessel steels classified as P-No 1 group 1 or 2 in Section 9 of the ASME Code and listed in Table 1 or 4 meet the requirement of Paragraph 5.2.1 in the as welded condition. Welding procedure qualifications, per API, ASME, or other appropriate specifications, shall be run on any welding procedure which is to be used. Welders using this procedure shall be familiar with the procedure and shall be capable of making welds which comply with the procedure.

5.2.1.2 Welding procedure qualifications on carbon steels, which use controls other than thermal stress relieving to control the hardness of the weldment, shall also include a hardness traverse across the weld HAZ and base metal to assure the procedure is capable of producing hardness of HRC 22 or less in the condition which it is to be used.

5.2.1.3 Low alloy steel a[illegible]sitic stainless steel weldments shall be stress relieved at a minimum temperature of 620 C (1150 F) to produce a hardness of HRC 22 or less.

5.3 Identification Stamping

5.3.1 Identification stamping [illegible] vibratory, and round V [illegible]

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[15] Copper base alloys may undergo accelerated weight loss corrosion in sour oil field environments particularly if oxygen is present.

[16] Welding electrodes with more than 1% nickel are not allowed for welding carbon and low alloy steels as indicated in Paragraph 3.3.1.

5.3.2 Conventional sharp V stamping is acceptable in low stress areas, such as the outside diameter of flanges. Sharp V stamping is not permitted in high stress areas unless subsequently stress relieved at 595 C (1100 F) minimum.

5.4 Threading

5.4.1 Machine Cut Threads

5.4.1.1 Machine cut threading processes are acceptable.

5.4.2 Cold Formed (Rolled) Threads

5.4.2.1 Subsequent to cold forming threads, the thread component shall meet the heat treat conditions and hardness requirements given in either Section 3 or 4 for the parent alloy from which the threaded component was fabricated. Depending upon the specific heat treat conditions and hardness limitations imposed on the parent alloy, post threading thermal treatments may be required.

5.5 Cold Deformation Processes

5.5.1 Cold deformation processes such as burnishing which do not impart cold work exceeding that incidental to normal machining operations such as turning or boring, rolling, threading, drilling, etc., are acceptable.

Section 6: Bolting

6.1 Exposed Bolting

6.1.1 Bolting which will be exposed directly to the sour environment or which will be buried, insulated, equipped with flange protectors or otherwise denied direct atmospheric exposure must be either a Class I or Class II material (See Paragraph 6.1.1.1 or 6.1.1.2).

NOTE. Designers and users should be aware that it may be necessary to derate the pressure rating in some cases when using low strength bolts. For API 6A flanges using Class II bolting, see API Standard 6A.

6.1.1.1 Class I Bolting

6.1.1.1.1 Acceptable bolting materials are listed in Tables 1, 2, and 3, and Sections 3 and 4.

6.1.1.1.2 Nuts shall meet the specifications of ASTM A-194 Gr 2M (HRC 22 maximum) or, alternatively, Paragraphs 6.1.1.1 or 6.1.1.2, as may be acceptable.

6.1.1.2 Class II Bolting

6.1.1.2.1 Bolting materials which meet the specifications of ASTM A-193 Gr B7M, 80,000 psi minimum yield strength and HRC 22 maximum are acceptable.

6.1.1.2.2 Nuts shall meet the specifications of ASTM A-194 Gr 2M (HRC 22 Maximum) as may be applicable.

6.2 Nonexposed Bolting

6.2.1 Class III Bolting

6.2.1.1 Nuts and bolts which are not directly exposed to sour environments and are not to be buried, insulated, equipped with flange protectors or otherwise denied direct atmospheric exposure, may be furnished to applicable Standards such as ASTM A-193 Gr B7.

Section 7: Plating and Coatings

Metallic materials shall meet the requirements of this section if they are to be exposed to sour environments (See Paragraph 1.3).

7.1 Metallic coatings (electroplated or electroless), conversion coatings, and plastic coatings or linings are not acceptable for preventing SCC of base metals. The use of such coatings for other purposes is outside the scope of this Standard.

7.2 Nitriding

7.2.1 Liquid or gas nitriding with a maximum case depth of 6 mils is an acceptable surface treatment when conducted at a temperature below the lower critical temperature of the alloy system being treated. Its use as a means of preventing SSC is not acceptable.

Section 8: Bearings, Springs, Pressure Measuring, and Sensing Devices

Metallic materials shall meet the requirements of this section if they are to be exposed to sour environments (See Paragraph 1.3).

8.1 Bearings

8.1.1 Bearings directly exposed to sour fluids shall be made from applicable materials listed in Tables 1, 2, and 3, and Sections 3 and 4. Bearings made from other metals must be isolated from the sour environment in order to function properly.

8.2 Springs

8.2.1 Springs directly exposed to the sour environment shall be made from applicable materials described in Sections 3 and 4 as listed in Tables 1, 2, and 3.

8.2.2 Co-Cr-Ni-Mo alloys, such as Elgiloy, may be used for springs in the cold worked and age hardened condition to its maximum hardness of HRC 60.

8.2.3 Springs from ASTM A 637 Grade 688 and Inconel X-750 are satisfactory in the cold worked and age hardened condition to a maximum hardness of HRC 50.

8.3 Pressure Measuring and Sensing Devices

8.3.1 Diaphragms and Pressure Seals(11) (14)

8.3.1.1 Diaphragms, pressure measuring devices, and pressure seals shall comply with Sections 3 and 4 and Tables 1, 2, and 3 or may be manufactured of Co-Cr-Ni-Mo alloys, such as Elgiloy and Havar to HRC 60.

8.4 Seal Rings

8.4.1 API compression seal rings made of centrifugally cast ASTM A-487 Grade CF8 or CF8M chemical compositions may be used in the "as cast" or annealed condition provided they are in accordance with the HB160 (HRB83) maximum hardness criteria.

Section 9: Valves and Chokes

Metallic materials shall meet the requirements of this section if they are to be exposed to sour environments (See Paragraph 1.3).

9.1 Valves and chokes shall be manufactured from materials in accordance with Sections 3 through 8 (See Paragraph 1.3).

Section 10: Wells, Flow Lines, Gathering Lines, Facilities, and Field Processing Plants

Metallic materials shall meet the requirements of this section if they are to be exposed to sour environments (See Paragraph 1.3).

10.1 Wells

10.1.1 Casing or Tubing

10.1.1.1 Casing or tubing directly exposed to sour environment (See Paragraph 1.3) shall meet the requirements of Table 4.

10.1.1.2 Casing which will not be exposed to sour fluids or which is exposed only to the controlled drilling fluid environment (See Paragraph 11.1.2) is outside the scope of this Standard.

10.2 Subsurface Equipment

10.2.1 Sucker Rod Pumps and Sucker Rods

10.2.1.1 Sucker rod pumps and rods are considered outside the scope of this Standard and are covered by other NACE and API Standards.

10.2.2 Gas Lift Equipment

10.2.2.1 Gas lift equipment normally handles gas which is free of H_2S. However, should sour gas (See Paragraph 1.3) be used, surface and subsurface equipment shall comply with Sections 3 through 8. Casing and tubing shall comply with Paragraph 10.1.1.

10.2.3 Other Artificial Lift Equipment

10.2.3.1 Other artificial lift equipment is outside the scope of this Standard.

10.2.4 Packers and Other Subsurface Equipment

10.2.4.1 Materials listed in Tables 1 through 5 and covered in Sections 3 through 8 are acceptable.

10.2.5 Slips

10.2.5.1 Slips are outside the scope of this Standard.

10.3 Wellheads

10.3.1 Wellhead components directly exposed to sour environments shall be manufactured in accordance with Sections 3 through 8. Wellhead components which are not directly exposed to the sour environment, or which are exposed to the controlled drilling environment (See Paragraph 11.1.2), are outside the scope of this Standard.

10.4 Flow Lines and Gathering Lines

10.4.1 The materials and fabrication procedures shall meet the requirements of Sections 3 through 8 and Tables 1 through 4.

10.5 Production Facilities

10.5.1 Oil and Gas Processing and Injection Facilities

10.5.1.1 Materials and fabrication procedures shall comply with Sections 3 through 8 and Tables 1 through 4.

10.5.2 Cryogenic Gas Processing Plants

10.5.2.1 The use of alloy steels containing more than approximately 1% nickel may be desirable in low temperature service to provide resistance to brittle fracture. Because of the absence of water, these alloys are acceptable in this service, provided adequate precautions (such as protecting the equipment by using inhibited methanol) are taken during startup and shutdown. Typical steels included in this class are: ASTM A-333 Grades 3, 4 7, 8, and 9, A-334; A-203; A-420 WPL 3, WPL 6, and WPL 8; A-350 LF 3; A-353, A-553, and A-552.

10.5.3 Water Injection and Water Disposal

10.5.3.1 Materials selection for water handling facilities is outside the scope of this Standard.

10.6 Compressor and Pumps

10.6.1 Materials exposed to the sour environment shall comply with Sections 3 through 8 and Tables 1 through 4 and/or Paragraph 10.6.2.

10.6.2 Gray cast iron (ASTM A-278 Class 35 or 40) and nodular iron (ASTM A-395) are acceptable as compressor cylinders, liners, pistons, and valves. Aluminum alloy 335, temper T-7 (ASTM B-26), is acceptable for pistons. Aluminum, soft carbon steel, and ARMCO iron are acceptable as gaskets in compressors handling sour gas.

10.6.3 AISI 4320 is acceptable for compressor impellers in the quenched and double tempered condition at a maximum yield strength of 90 ksi. Both tempers shall be conducted below the lower critical temperature and above a minimum of 620 C (1150 F). The second tempering temperature shall be lower than the first tempering temperature.

Section 11. Drilling and Well Servicing Equipment

Metallic materials shall meet the requirements of this section if they are to be exposed to uncontrolled sour environments (See Paragraph 1.3).

11.1 Control of Drilling and Well Servicing Environments

11.1.1 The service stresses involved in drilling and well servicing operations often require materials and components having hardness (strengths) greater than permitted for carbon and low alloy steels in Section 3 and Table 1. When such materials and components are required for drilling formations or operating in environments containing H_2S, the primary means for avoiding SSC is by control of the drilling or well servicing environment. As service stresses and material hardness increase, drilling fluid control becomes increasingly important.

11.1.2 The drilling environment is controlled by maintenance of drilling fluid hydrostatic head and fluid density to minimize formation fluid in-flow and by the use of one or more of the following: (1) Maintenance of pH 10 or higher to neutralize H_2S in the drilled formation, (2) use of chemical sulfide scavengers, and (3) use of a drilling fluid in which oil is the continuous phase.

11.2 Drilling Equipment

11.2.1 Drill Stem

11.2.1.1 Drill pipe, tool joints, drill collars, and other tubular components.

11.2.1.1.1 Tubular components meeting API specifications listed in Table 4 are acceptable if the drilling environment is controlled (See Paragraph 11.1). For optimum SSC resistance, steel components having specified minimum yield strengths greater than 95 ksi should be heat treated by quenching and tempering.

11.2.1.1.2 When aluminum drill pipe is used, the drilling fluid pH should not exceed 10.5 to avoid accelerated weight loss corrosion.

11.2.1.2 Welding of Tool Joints to Drill Pipe

11.2.1.2.1 The weld and heat affected zone (HAZ) shall be heat treated by austenitizing, cooling to a temperature below the transformation range and tempering at a minimum tempering temperature of 595 C (1100 F).

11.2.1.3 Hardsurfacing

11.2.1.3.1 Hardsurfacing deposits on tubular drilling components may be applied only to thick sections where service stresses are lower and do not require heat treatment after being applied

11.2.2 Drill Bits

11.2.2.1 Drill bits are outside the scope of this Standard

11.2.3 Other Drilling Components

11.2.3.1 Other drilling components (swivels, kelly cocks, etc.) shall be made from materials shown in Table 1. Parts of these components which are isolated from the sour drilling fluid or which are exposed only to the controlled drilling fluid environment (See Paragraph 11.1.2) are outside the scope of this Standard

11.3 Blowout Preventers (BOP)

11.3.1 Blowout preventer [illegible] excluding [illegible] Sections 3 through 8

11.3.2 Blowout Preventer Shear Blades

11.3.2.1 High strength and high hardness steels are required for ram shear blades to shear drill pipe during drilling emergency conditions. However, the user shall be advised that these materials are highly susceptible to SSC.

11.3.3 Rams

11.3.3.1 Low alloy steels, listed in Table 1 and processed per Sections 3 through 8, are acceptable for rams.

Low alloy steels in the Cr Mo class (and its modifications) are acceptable as rams at a maximum hardness of HRC 26 in the quenched and tempered condition. Careful attention to chemical composition and heat treatment is required to insure SSC resistance of these alloys at hardness levels greater than HRC 22. SSC tests shall be conducted to establish that the material is equivalent in SSC performance to materials which have given satisfactory service in sour environments. (See Tables 1 through 4 and Sections 3 through 8)

11.4 Choke Manifold and Kill Lines

11.4.1 Choke manifolds and kill lines shall comply with Sections 3 through 8

11.5 Slush Pumps

11.5.1 Slush pumps are exposed only to controlled environment drilling fluids (See Paragraph 11.1.2) and are outside the scope of this Standard

11.6 Drill Stem Testing

11.6.1 Drill stem testing is not ordinarily conducted in a controlled drilling environment. Materials for drill stem testing shall comply with the requirements of Sections 3 through 8 and Paragraphs 10.1 and 10.2 when testing without a controlled drilling environment

Materials shown in Table 4 can also be used with operational procedures that consider the factors enumerated in Paragraph 1.3 which may involve use of inhibitors, limited entry, limited time, limited pressure, metallurgical or design factors. Such operational procedures are outside the scope of this Standard (See API RP 7G and API RP 49)

11.7 Formation Testing Tools

11.7.1 Materials for formation testing tools shall [illegible] Sections 3 through 8 and Paragraphs [illegible]

11.8 Floating Drilling Operations

11.8.1 Blowout Preventers

11.8.1.1 Blowout preventers shall comply with Paragraph 11.3

11.8.2 Drilling Riser Systems

11.8.2.1 If the flow of sour formation fluids is handled by diverting the flow at the seafloor BOP through the choke and kill lines, the drilling riser pipe, riser connections, ball or flex joints, and telescoping joints need not comply with this Standard If, however, the riser system is to be exposed to sour environments (See Paragraph 1.3), materials shall meet the requirements of Sections 3 through 8 and Paragraph 10.1.1.1

11.8.3 Choke and Kill Lines

11.8.3.1 Materials for the choke and kill lines and manifolds shall comply with Sections 3 through 8

11.9 Well Servicing Equipment

11.9.1 Work String

11.9.1.1 Work strings used during well servicing when sour fluids are to be encountered shall comply with Paragraph 10.1.1. Work strings which are to be exposed to controlled drilling fluid environments (See Paragraph 11.1.2) only, are outside the scope of this Standard

11.9.2 Blowout Preventers

11.9.2.1 Blowout preventers shall comply with Paragraph 11.3.

11.9.3 Choke and Kill Lines

11.9.3.1 Choke and kill lines and mainfolds shall comply with Sections 3 through 8.

11.9.4 Production Test Facilities

11.9.4.1 Production test facilities shall comply with Sections 3 through 8

11.9.5 Wire Line Lubricator Assembly

11.9.5.1 Wire line lubricator and auxiliary equipment shall comply with Sections 3 through 8 and Paragraph 10.1.1.1

Exposure to Sour Environment (See Paragraph 1.3)

Materials listed in this table should be used only under conditions noted in the text of this Standard

Application	Carbon Steels	Low Alloy Steels	Other
General	AISI 1010 thru 1045 API 6A Type 1 & 4 CSA G 40 21	AISI 4130 thru 4145 8620 thru 8645 8720 thru 8745 API 6A Type 2 & 3 ASTM A 182 Gr F 22	
Pipe	ASTM A 671 CA 55, CB & CC 60 CD 70, 80 CE 55, 60 A 672(1)	ASTM A 155	
Tubes	ASTM A 161 LC A 179 A 214 A 334 Gr 1 & 6 A 556 Gr A2 & B2	ASTM A 161 T1	
Plates and Sheets	ASTM A 36 A 131 A 283 A 285 A, B, & C A 299 A 442 Gr 55 & 60 A 515 A 516 A 537 Cl 1 & 2 A 569 A 570 A 573 A 662 A 678 CSA G 40 8	ASTM A 202 A 204 A 255 Gr A & B A 387 A 441 A 633 Gr A, B A 633 Gr A, B, C D & E	
Bar Stock	ASTM A 575 Gr 1020 thru 1030(1) A 576 Gr 1020 thru 1030(1)		
Bolting	ASTM A 194 Gr 2M A 307 Gr B(2) AISI 1036 (Normalized)	ASTM A 193 Gr B7M (22 HRC Max) A 320 Gr L7M (22 HRC Max)	
Castings	ASTM A 216 Gr WCA, WCB, WCC A 352 LCA, LCB, LCC API 6A Type 1 & 4	ASTM A 217 Gr WC 1 A 487 Gr 1, 2, 4, 8, 9 A 352 LC 1 API 6A Type 2 & 3	ASTM A 395
Fabricated and Welded Fittings	ASTM A 105 A 181 Gr 1 & 2 A 182 Gr F1 A 234 WPA, WPB, WPC A 350 LF 1 & LF 2 A 381 Cl 1 Y35 thru Y60 A 420 WPL 6 A 541 Cl 1	ASTM A 182 F1 & F2 A 541 Cl 4, 5, 6 API 6A	
Compressor	All components exposed to wet(4) sour gas shall be heat treated if necessary to a maximum yield strength of 90,000 psi		ASTM A 278 Cl 35 or 40 A 395

(1) Resulfurized grades not acceptable

(2) Annealed and normalized after fabrication if cold headed

(3) All grades except H80 are acceptable. H80 is acceptable when manufactured from ASTM A 302 Grade B only

(4) Contains liquid water

TABLE 2 – Stainless Steels Acceptable for Direct Exposure to Sour Environment (See Paragraph 1.3)

Note: Materials listed in this table should be used only under conditions noted in the text of this Standard. Tradenames are given for alloy recognition and are not intended to limit source selection.

Ferritic	Martensitic	Precipitation Hardening	Austenitic	Duplex (Austenitic/Ferritic)
AISI 405 430	AISI 410 501	ASTM A 453 Gr 660(2) (A 286) A 638 Gr 660(2) (A 286)	Alloy 20Cb3 AISI 302 304 304L 308 309 310 316 316L 317 321 347	Sandvik SAF 2205 Mannesmann AF 22
ASTM A 268 TP 405 TP 430 TPXM 27 TPXM 33	ASTM A 217 Gr CA 15 A 268 TP 410 A 296 Gr CA 15M A 487 Gr CA 15M	17-4PH (UNS S17400)	ASTM A 182 A 193(1) Gr B8, B8M B8MA A 194(1) Gr 8A, 8MA A 320(1) Gr B8, B8M A 351 Gr CF3, CF8 CF3M, CF8M B 463 B 473	

TABLE 3 – Nonferrous Materials Acceptable for Direct Exposure to Sour Environment (See Paragraph 1.3)

Materials listed in this table should be used only under the conditions noted in the text of this Standard
Tradenames are intended for alloy recognition and are not intended to limit source selection

Nickel-Copper Alloy		Nickel-Chromium-Iron Alloy		Nickel-Chromium-Molybdenum Alloys				
UNS[1] N04400		UNS N06600		UNS N06225		UNS N10002		UNS N10276
(Monel Alloy 400)		(Inconel Alloy 600)		(Inconel 625)		(Hastelloy C)		(Hastelloy C 276)
ASTM	SAE AMS	ASTM	SAE AMS	ASTM	SAE AMS	ASTM	SAE AMS	ASTM
B127	4544	B153	5540	B443	5581	A567	5388	B366
B163	4574	B166	5580	B444	5599	Gr 4	5389	B574
B164	4575	B167	5665	B446	5666	34	5530	B575
B366	4730	B366	7232		5837	B336	5750	B619
B564	4731	B516						B622
	7233	B517						B626
		B564						

				Hastelloy G				
UNS N05500	UNS N07750			UNS N07718		UNS N06002		
(Monel Alloy K500)	(Inconel Alloy X 750)			(Inconel Alloy 718)		(Hastelloy X)		
SAE AMS	ASTM	SAE AMS		ASTM	SAE AMS	ASTM	SAE AMS	
4676	A637	5542	5669	A637	5383	A567	5390	5754
		5582	5670	A670	5589	Gr 5	5536	5798
		5598	5671		5590	B435	5587	5799
		5667	5698		5596	B572	5588	7237
		5668	5699		5597			
					5662			
					5663			
					5664			
					5832			
ASTM				ASTM				
A494				A494 Gr CW 12 M1				
Gr M35				Gr CW 12 M2				

Nickel Iron Chromium Alloys		Cobalt-Nickel-Chromium Molybdenum Alloys	Other Alloys	Coatings and Overlays
UNS N08800		MP35N (UNS R30035)	Aluminum Base Alloys	Co-Cr-W (Stellite Alloys)
(Incoloy 800)		Elgiloy (UNS R30003)	Copper Base Alloys	Ni-Cr-B (Colmonoy Alloys)
ASTM	SAE AMS	Havar (UNS R30004)	Cobalt Nickel Chromium Tungsten Alloys UNS R30605 (Cyclops L605) (Haynes Alloy No 25)	Ni-B (Ancorspray Alloys)
B163	5766			Cast, Cemented, or Thermally Sprayed Powder Tungsten Carbides
B366	5871			Cast or Thermally Sprayed Powdered Ceramics
B407				
B408				
B409				
B514				
B515				
B564				
(Incoloy 825)				
ASTM				
B163	B424			
B423	B425			

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[1] Unified numbering system for metals and alloys ASTM E527 or SAE J1086

[2] Aerospace Materials Specifications Society of Automotive Engineers, Inc , 400 Commonwealth Drive, Warrendale, Pennsylvania 15096

TABLE 4 – Acceptable API and ASTM Specifications for Tubular Goods

All materials listed in Tables 1 through 3 are acceptable
Materials listed in this table are acceptable under environmental conditions noted

Operating Temperature		
For All Temperatures(1)	For 65 C (150 F) or Greater(2)	For 80 C (175 F) or Greater
Tubing and Casing API Spec 5A Gr H-40,(3) J-55 & K-55 5AC Gr C-75 & L-80 Proprietary Grades per Paragraph 3.3.3	**Tubing and Casing** API Spec 5A Gr N-80 (Q&T) 5AC Gr C-95 Proprietary Q&T Grades with 110 ksi or less maximum yield strength	**Tubing and Casing** API Spec 5A Gr H-40 & N-80 5AX Gr P-105 & P-110 Proprietary Q & T Grades to 140 ksi maximum yield strength
Pipe(4) API Spec 5L Gr A & B 5LS Gr X-43 thru X-65(7) 5LX Gr X-42 thru X-65(7) ASTM A-53 A-106 Gr A, B, C A-333 Gr 1 & 6 A-524 Gr 1 & 2 A-381 Cl 1 Y35-Y65(7)		
Drill Stem Materials(5) API Spec 5A Gr D & E 5AX Gr X-95, G-105, S-135 (See 11.2.1.1) API Spec 7 Aluminum 2014-T6 (UNS A92014)(6)		

(1) Impact resistance may be required by other standards and codes for low operating temperatures

(2) Continuous minimum temperature; for lower temperatures, select from column 1

(3) 80 ksi maximum yield strength permissible (latest revision of API 5A includes this requirement)

(4) Welded grades must meet the requirements of Sections 3 through 8

(5) For use under controlled environments as defined in Paragraph 11.1.2

(6) Maximum drilling fluid pH = 10.5

(7) Grades X-56 through X-65 and Y56 through Y-65 shall have a maximum hardness of HRC 22

TABLE 5 – Acceptable Materials for Subsurface Equipment for Direct Exposure to Sour Environment (See Paragraph 1.3)

All materials listed in Tables 1 through 4 are acceptable

Use	Material
Drillable packer components	Ductile Iron (ASTM A-536, A-571)
Drillable packer components	Malleable Iron (ASTM A-220, A-602)
Compression members	Gray Iron (ASTM A-48, A-278)
All	9Cr-1Mo (ASTM A-199 Gr T9, A-200 Gr T9, A-296 Gr 9, A-182 Gr F9)(1) ASTM A-213 T9

(1) Maximum hardness of HRC 22

Appendix A

The 17Cr-4Ni precipitation hardening stainless steel is acceptable in SSC service when heat treated to a hardness range of 29 to 33 HRC by one of the following heat treating procedures.

Procedure 1

1 Solution treated at 1040 C (1900 F) and quench in oil. Furnace must be at 1040 C (1900 F) before loading parts. This steel must be heated rapidly through the range of 840 to 950 C (1550 to 1750 F).

2 Cool material to below 32 C (90 F) before precipitation hardening.

3 Harden at 620 C (1150 F) for 4 hours and cool in air.

4 Cool material to below 32 C (90 F) before second hardening cycle.

5 Harden at 620 C (1150 F) for 4 hours and cool in air.

6 Check hardness.

Procedure 2

1 Solution treat at 1040 C (1900 F) and quench in oil. Furnace must be at 1040 C (1900 F) before loading parts. This steel must be heated rapidly through the range of 840 to 950 C (1550 to 1750 F).

2 Cool material to below 32 C (90 F) before precipitation hardening.

3 Harden at 760 C (1400 F) for 2 hours and air cool.

4 Cool material to below 32 C (90 F) before second hardening cycle.

5 Harden at 620 C (1150 F) for 4 hours and air cool.

6 Check hardness.

Appendix B — Alphabetical Listing of Trade Names and Trade Marks

Alloy 20Cb3, Pyromet 31
Carpenter Technology Corporation
Reading, Pennsylvania 19603

Ancorsprays
Hoeganaes Corporation
Riverton, New Jersey 08077

Colmonoy
Wall Colmonoy Company
Detroit Michigan 48203

Elgiloy
Elgiloy Company
Elgin, Illinois 60120

Hastelloy, Haynes Alloy, Multimet & Stellite
Cabot Corporation
Stellite Division
Kokomo, Indiana 46901

Havar
Hamilton Technology, Incorporated
Lancaster, Pennsylvania 17604

Inconel, Incoloy, Monel, Nimonic
Huntington Alloys, Incorporated
Huntington, West Virginia 25720

MP35N
Standard Pressed Steel Company
Jenkintown, Pennsylvania 19046

Appendix C
PH15-7Mo Snap Rings for SSC Service

Snap rings processed from PH15-7Mo in the RH950 solution annealed and aged at 510 C (950 F) condition and heat treated as described below are acceptable at HRC 30-32.

1 Temper at 620 C (1150 F) for 4 hours, 15 minutes. Cool to room temperature in still air.

2 Retemper at 620 C (1150 F) for 4 hours, 15 minutes. Cool to room temperature in still air.

3 Temper at 560 C (1050 F) for 4 hours, 15 minutes. Cool to room temperature in still air.

4 Check hardness, HRC 30-32.

Supplement Issued for NACE Standard MR-01-75 (1980 Revision)

Supplement No. 1, dated September, 1980, has been issued for NACE Standard MR-01-75 (1980 Revision), "Sulfide Stress Cracking Resistant Metallic Materials for Oilfield Equipment."

The supplement presents several editorial revisions as well as two substantive changes to the Standard. One substantive change is the addition of a paragraph and tabular data concerning nickel-chromium-molybdenum-aluminum-titanium-columbium alloy UNS N07031. The other

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Supplement No. 1 issued for MR-01-75 (1984 Editorial Revision)

NACE Standard MR-01-75 (1984 Editorial Revision), "Sulfide Stress Cracking Resistant Metallic Material for Oilfield Equipment," was recently finalized and is now available from NACE. A supplement to the revised standard was also approved in January 1985, by letter ballot following the resolution of three negative votes cast in the November 1983 balloting. Final approvals for Supplement No. 1 were received by the T-1F Unit Committee chairman, the T-1 Group Committee chairman, and the Technical Practices Committee chairman.

The supplement adds a new paragraph to Section 4, Nonferrous Metals, which reads:

"4.4.1.3 Commercially pure tantalum (UNS RO5200) in the annealed and gas tungsten arc welded-annealed conditions is acceptable to a maximum hardness of HRB 55."

The supplement also includes an addition to Table 3 under the heading "Other Alloys":

"UNS RO5200"

Either the full text of the standard with the supplement or additional copies of the supplement may be purchased from NACE. For more information, contact NACE Publications Order Department, P.O. Box 218340, Houston, TX 77218; telephone (713)492-0535.

MR-01-75 Supplements issued

The second and third supplements to NACE Standard MR-01-75 (1984 Editorial Revision), "Sulfide Stress Cracking Resistant Metallic Materials for Oilfield Equipment," were recently approved by officers of Group Committee T-1 and the TPC Chairman. Supplement #2 was completed in February, and Supplement #3 was completed in March.

Supplement #2 includes six revisions, the first of which is an important editorial revision which corrects the erroneous inclusion of UNS R30004 in paragraph 8.3.2 of the standard. Task Group T-1F-1, which is responsible for MR-01-75, noted that the alloy was incorrectly included during the 1984 Editorial Rewrite of the Standard and determined that UNS R30004 should not be listed for applications noted within paragraph 8.3.2. Task group research has shown that the alloy was never balloted at HRC 60 for spring service applications. The correct version of the paragraph should read:

> "8.3.2 Cobalt-chromium-nickel-molybdenum alloy UNS R30003 may be used for springs in the cold worked and age hardened condition to HRC 60 maximum."

The remainder of Supplement #2 was approved following the resolution of negatives votes cast in the November, 1983 ballot for inclusion of materials in MR-01-75. The revisions are:

1. Add Paragraph 4.4.1.4, Titanium Alloys, as follows: "Specific guidelines must be followed for successful applications of each titanium alloy specified in this standard. For example, hydrogen embrittlement of titanium alloys may occur if galvanically coupled to certain active metals (e.g. carbon steel) in H_2S-containing aqueous media at temperatures greater than 80 C. Some titanium alloys may be susceptible to crevice corrosion and/or stress corrosion cracking in chloride environments. Hardness has not been shown to correlate with susceptibility to sulfide stress cracking. However, hardness has been included for alloys with high strength to indicate the maximum testing levels where failure has not occurred."
2. Add Paragraph 4.4.1.4.1, as follows: "Titanium alloy UNS R53400 in the annealed condition. Heat treatment shall be annealing at 774 C (1425 F) ± 14 C (25 F) for two hours followed by air cool. Maximum hardness to be HRB 92."
3. Add Paragraph 4.4.1.4.2, as follows: "Titanium alloy UNS R58640 up to hardness maximum HRC 42."
4. Revise Paragraph 4.2.5.1, as follows: "Nickel-Chromium-Molybdenum-Alloys UNS N06625, UNS N10002, UNS N06007, UNS N06002, and UNS N06985."
5. Add to Table 3, under the heading, "Nickel-Chromium Molybdenum Alloys": "UNS N06985."

Supplement #3, which was also approved following the resolution of negative votes from the November, 1983 ballot, includes two revisions to the standard:

1. Add Paragraph 4.4.1.4.3, as follows: "Titanium alloy UNS R50400 up to hardness maximum HRB 100."
2. Add to Table 2 under the heading, "Duplex (Austenitic/Ferritic)": "UNS S32550, wrought condition only^3" Add footnote: "^{3}Aging over 500 F may reduce low temperature toughness and reduce resistance to environmental cracking."

Either the full text of the standard with the supplements or additional copies of the supplement may be purchased from the NACE Publications Order Department, P.O. Box 218340, Houston, TX 77218.

Revisions Approved for MR-01-75

The Board of Directors ratified three revisions to NACE Standard MR-01-75 (1980 Revision and Supplement). The standard, "Sulfide Stress Cracking Resistant Metallic Materials for Oil Field Equipment," is among the most used of NACE Material Requirement standards.

The revisions, which are now officially integral parts of the standard are:

1. Add UNS N04405 to Table 3, under the heading, "Nickel-Copper Alloy."
2. Add Paragraphs 4.4,4.4.1, and 4.4.1.1 as follows:

"4.4 Special condition usage alloys listed in this section are acceptable when they satisfy the special conditions noted for each alloy.

4.4.1 Nickel-Chromium-Molybdenum Alloy.(9)

4.4.1.1 Nickel-Chromium-Molybdenum-Tungsten Alloys (such as UNS N10276) are acceptable in the cold worked and unaged condition at a maximum hardness of HRC 45 when used at a minimum temperature of 250 F."

3. Revise Appendix A (as shown in the Standard and its supplement) to read as follows:

Appendix A

The 17 Cr-4 Ni precipitation hardening stainless steel is acceptable in SCC service when heat treated to a maximum hardness of HRC 33 by one of the following procedures:

Procedure 1 (Double age at 1150 F)

(1) Solution anneal at 1040 C (1900 F) and air cool or oil quench to below 32 C (90 F).

(2) Harden at 620 C (1150 F) for four (4) hours at temperature and cool in air.

(3) Cool material to below 32 C (90 F) before the second precipitation hardening step.

(4) Harden at 620 C (1150 F) for four (4) hours at temperature and cool in air.

Supplement No. 4 to MR-01-75

An additional revision to NACE Standard MR-01-75 (1980 Revision), "Sulfide Stress Cracking Resistant Metallic Materials for Oilfield Equipment," has been approved as Supplement No. 4.

4.1.4.3 Nickel-Chromium-Molybdenum-Aluminum-Titanium-Columbium Alloy UNS N07031 is acceptable in the solution annealed condition at a maximum hardness of 35 HRC. This material is also acceptable when solution annealed plus aged at 1400/1600 F for 4 hours maximum to a maximum hardness of HRC 40.

Revision to MR-01-75 Issued as Supplement

Supplement No. 5 to NACE Standard MR-01-75 "Sulfide Stress Cracking Resistant Metallic Material for Oilfield Equipment" has been issued. The supplement, which includes one revision to the Standard, will be provided to all members of NACE Group Committee T-1 on Corrosion Control in Petroleum Production. Others may order the supplement from the NACE Publications Order Department.

The revision, which modifies paragraph 4.1.4.2 reads as follows:

4.1.4.2 Nickel-chromium-molybdenum-aluminum alloys (such as UNS N07718) in the solution-annealed, hot rolled, or hot rolled and aged conditions are acceptable to a maximum hardness of HRC 35. The nickel-chromium-molybdenum-aluminum alloy UNS N07718 in the solution-annealed and aged condition is acceptable to a maximum hardness of HRC 40.

MR-01-75 supplement No. 5 issued

The fifth supplement to NACE Standard MR-01-75 (1984 Editorial Revision), "Sulfide Stress Cracking Resistant Metallic Materials for Oilfield Equipment," was recently approved. The items listed in the supplement were processed in accordance with NACE's consensus approval procedure and reviewed and voted upon by members of NACE Group Committee T-1 on Corrosion Control in Petroleum Production. The supplement consists of seven revisions. Publication approval was given by T-1F Unit Committee Chairman John A. Straatmann (Climax Molybdenum Company, Bridgeville, PA), T-1 Group Committee Chairman James E. Donham (Welchem, Inc., Houston, TX), and Technical Practices Committee Chairman Lyle D. Perrigo (Battelle Alaska Operations, Anchorage, AK) following the resolution of negative votes cast in the November, 1983 and November, 1984 ballots for inclusion of materials in MR-01-75. The revisions are:

1. Add paragraph 3.6.3, as follows:

> "Austenitic stainless steel alloy UNS N08020 is acceptable in the annealed or cold worked condition at a hardness level of HRC 32 maximum."

2. Revise paragraph 4.2.3.2, as follows:

> "Nickel-iron-chromium-molybdenum alloy UNS N09925 in the solution annealed or cold worked condition is acceptable to a maximum hardness of HRC 35, in the solution annealed and aged condition is acceptable to a maximum hardness of HRC 38, and in the cold worked and aged and in the hot finished and aged conditions is acceptable to a maximum of HRC 40."

3. Add paragraph 4.2.3.3, as follows:

> "Nickel-Iron-Chromium-Molybdenum alloy UNS N08024 to HRC 32 maximum."

4. Add to Table 3, under the heading, "Other Alloys":

> "UNS N08024"

5. Revise Section 8 title, as follows:

> "Bearings, Springs, Pressure Measuring and Sensing Devices, and Bearing Pins"

6. Add paragraph 8.6, as follows:

> "Bearing Pins"

7. Add paragraph 8.6.1, as follows:

> "Bearing pins, e.g., core roll pins made from UNS N10276 in the cold worked condition with a maximum hardness of HRC 45, may be used."

The full text of the standard with all five supplements or additional copies of the supplements may be purchased from the NACE Publication Orders Department, P.O. Box 218340, Houston, TX 77218; telephone (713) 492-0535.

Revision to MR-01-75 Issued As Supplement

Supplement No. 6 to NACE Standard MR-01-75 (1980 Revision), "Sulfide Stress Cracking Resistant Metallic Material for Oilfield Equipment," is now available from the NACE Publications Order Dept., P.O. Box 218340, Houston, TX 77218.

The supplement includes two revisions to the Standard, as follows:

Add paragraph 4.1.2.3:

> 4.1.2.3 Nickel-iron-chromium-molybdenum alloy UNS N09925 in the solution annealed, cold worked and aged, or solution annealed and aged conditions.

Revise step 1 of Procedures 1 and 2 in Appendix A, as revised previously in Supplements 2 and 3, to read as follows:

> (1) Solution anneal at 1900 F (1040 C) and air cook, or suitable liquid quench, to below 90 F (32 C).

MR-01-75 revision issued as supplement

A revision to NACE Standard MR-01-75, "Sulfide Stress Cracking Resistant Metallic Material for Oilfield Equipment," was approved recently by letter ballot following the resolution of three negative votes cast in the November 1983 balloting. Final approval by the Unit Committee T-1F chairman, the Group Committee T-1 chairman, and the Technical Practices Committee chairman came in July of this year.

The supplement includes the addition of a new paragraph to Section 9, to read as follows:

> 9.2 Shafts, Stems, and Pins
>
> 9.2.1 Austenitic Stainless Steel UNS S20910 is acceptable for valve shafts, stems, and pins at a hardness level of HRC 35 maximum in the cold worked condition provided this cold working is preceded by an anneal.

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following the resolution of negative votes cast in the November 1984 ballot of items for inclusion in MR0175-84.

The three revisions included in Supplement #7 are:

1. Revise paragraph 4.2 as follows (revision underlined):

   "Alloys listed in this section and in Table 3 are acceptable in conditions noted under each metal at HRC 35 maximum unless hardness maximum is specified otherwise."

2. Add paragraph 4.2.3.3 to read as follows:

   "Nickel-iron-chromium molybdenum alloy UNS N08028, listed in Table 3, is acceptable in the solution annealed and cold worked condition to HRC 33 maximum."

3. Add to Table 3 under heading, "Nickel-Iron-Chromium-Molybdenum Alloys:" UNS N08028."

Supplement #8 revises paragraph 4.2.5.1 to read, "4.2.5.1.1 Nickel-chromium-molybdenum-aluminum alloy UNS N06110 in the annealed or cold-worked conditions to HRC 40 maximum."

Supplement approved to MR-01-75

The sixth supplement to NACE Standard MR-01-75 (1984 Editorial Revision), "Sulfide Stress Cracking Resistant Metallic Materials for Oilfield Equipment," was recently approved. The supplement consists of four technical revisions that were processed in accordance with NACE's consensus approval procedure and reviewed and voted upon by members of NACE Group Committee T-1 on Corrosion Cntrol in Petroleum Production, and two editorial revisions that were reviewed and approved in accordance with Section 8 of the NACE **Standard Manual.**

Publication approval was given by the T-1F Unit Committee Chairman, John A. Straatmann (Climax Molybdenum Company, Bridgeville, PA), the T-1 Group Committee Chairman, James E. Donham (Welchem, Inc., Houston, TX), and the Technical Practices Committee Chairman, Lyle D 'errigo (University of Alaska - AEIDC, Anchorage, AK) following the resolution of negative votes cast in the November 1983 ballot for inclusion of materials in MR-01-75.

The technical revisions are:

1. Add paragraph 3.11.2, as follows:

   "Cast Duplex (Austenitic/Ferritic) Stainless Steel

   Cast Duplex (Austenitic/Ferritic) stainless steel Z 6CNDU20.08M NF A 320-55-French National Standard is acceptable at hardness levels of 17 HRC maximum in the annealed and quenched condition provided the ferrite content is in the range of 25 to 40%. The annealing shall be at a temperature of 1150 C ± 10 C (2100 F ± 20 F) and shall be followed by a rapid quench to avoid the precipitation of sigma phase.[6]"

2. Add to Table 2:

   "Cast Duplex (Austenitic/Ferritic) Stainless Steel Z 6CNDU20.08M, NF A 320-55-French National Standard"

3. Add paragraph 4.4.1.4.4, as follows:

   "Titanium Alloy UNS R56260 in the annealed, solution annealed and solution treated and aged condition is acceptable up to a hardness maximum of HRC 45."

4. Add to Table 3, under the heading, "Other Alloys":

   "Titanium Alloy UNS R56260"

The editorial revisions are:

1. Revise paragraph 6.2.1.1.2, as follows:

   "Nuts shall meet the specifications of ASTM A 194 Grade 2HM (HRC 22 maximum) or alternatively, paragraphs 6.2.1.1 or 6.2.1.2, as may be acceptable."

2. Revise Supplement Number 5 (July 1985), Revision 4, as follows:

   "4) Add to Table 3, under the heading, 'Nickel-Iron-Chromium Alloys': 'UNS N08024'"

Supplement to MR0175-84 approved for publication

A revision to paragraph 10.7.3 of NACE Standard MR0175-84, "Sulfide Stress Cracking Resistant Metallic Materials for Use in Oilfield Equipment," has been approved for publication via the NACE consensus review and approval process. The revision is designated as Supplement #9 to MR0175-84 and reads as follows (the underlined portion designates the revision):

10.7.3 AISI 4320 and a modified version of 4320 which contains 0.28 to 0.33% carbon are acceptable for compressor impellers in the quenched and double tempered condition at a maximum yield strength of 90 ksi (620 MPa). Both tempers shall be conducted below the lower critical temperature and above a minimum of 1150 F (620 C). The second tempering temperature shall be lower than the first."

The revision was balloted in December 1986 and approved by members of NACE Group Committee T-1 on Corrosion Control in Petroleum Production and the chairmen of NACE Unit Committee T-1F, Group Committee T-1, and the Technical Practices Committee.

Proposed revisions and additions to MR0175-85 are balloted annually with the approval of NACE Task Group T-1F-1. For more information, contact the Technical Activities Department at NACE Headquarters in Houston.■

NACE committees approve MR0175-84 Supplement

An addition to Paragraph 4.2.5 of NACE Standard MR0175-84, "Sulfide Stress Cracking Resistant Metallic Materials for Use in Oilfield Equipment," has been approved for publication via the NACE consensus review and approval process. The standard revision is designated as Supplement #11 to MR0175-84 and reads as follows:

"4.2.5.5 UNS N07716 to HRC 40 maximum in the solution annealed and aged condition." UNS N07716 will also be added to the section titled "Nickel-Chromium-Molybdenum Alloys," in Table 3.

The new paragraph was balloted in January 1988 and approved by members of NACE Group Committee T-1 on Corrosion Control in Petroleum Production and the chairmen of NACE Unit Committee T-1F, Group Committee T-1 and the Technical Practices Committee.

Proposed revisions and additions to MR0175-85 are balloted annually with the approval of NACE Task Group T-1F-1. For more information, contact the NACE Technical Activities Department at (713) 492-0535. ■

Procedures to revise MR0175-84 implemented

Beginning in 1989, a revised MR0175 standard, "Sulfide Stress Cracking Resistant Metallic Materials for Oilfield Use," will be issued once each year. The revisions to the standard will be either editorial revisions deemed necessary by NACE Task Group T-1F-1 or technical revisions that have been approved via a ballot of members of Group Committee T-1 on Corrosion Control in the Petroleum Production. T-1F-1, led by Chairman David Patrick (ARCO Exploration and Technology, Plano, TX) and Vice Chairman Michael Hartmann (Cameron Iron Works Inc., Houston), is the NACE technical committee that oversees proposed revisions to MR0175-84.

In the past, technical revisions to MR0175-84 have been issued in the form of separate supplements and were not incorporated into the actual document until a revision was published. With the new distribution system, MR0175 supplements will be eliminated. As soon as a technical revision is approved, a notice will be sent to T-1 members and placed in *Materials Performance*; the revision then will be incorporated in the next MR0175 edition to be printed within one year of the revision. The revision will not be sold as a supplement to the standard prior to publication of the next edition.

In addition, Task Group T-1F-1 will sponsor a ballot during the Fall/Winter months of each year. Anyone interested in proposing a revision to MR0175-84 may submit the appropriate material for inclusion in a ballot (Forms are available from the NACE Technical Activities Department.) The deadline for submitting material is strictly enforced and usually occurs three months prior to the next ballot. Information on balloting deadlines is available from the NACE Technical Activities Department.

A major editorial rewrite of MR0175-84 is expected to be pub lished in early 1989. The current 12 supplements to MR0175-84 will be incorporated into the document at that time. The editorial rewrite was sent for letter ballot to T-1 members in September 1986 to ensure that the proposed editorial revisions were not technical.

Supplements 9, 10, 11, and 12 to the standard were approved in 1988. They are as follows:

Supplement #9—Revise Paragraph 10.7.3 as follows (revision is italicized): "10.7.3 AISI 4320 *and a modified version of 4320 which contains 0.28 to 0.33 carbon are* acceptable for compressor impellers in the quenched and double tempered condition at a maximum yield strength of 90 ksi (620 MPa). Both tempers shall be conducted below the lower critical temperature and above a minimum of 1150 F (620 C). The second tempering temperature shall be lower than the first." (approved June 1988)

Supplement #10—Revise Paragraph 8.3.2 as follows (revision is italicized): "8.3.2 Cobalt-chromium-nickel-molybdenum alloy UNS R30003 may be used for springs in the cold worked and age hardened condition to HRC 60 maximum. *UNS R30035 may be used for springs in the cold worked and age hardened condition to HRC 55 maximum when aged for a minimum of four (4) hours at a temperature no less than 1200 F (648 C)*." (approved June 1988)

Supplement #11—Add Paragraph 4.2.5.5 to read as follows: "4.2.5.5 UNS N07716 to HRC 40 maximum in the solution-annealed and aged condition." Add UNS N07716 to the section titled "Nickel-Chromium-Molybdenum Alloys," in Table 3 (approved August 1988).

Supplement #12—Add Paragraph 8.8 on Duplex Stainless Steel for Wellhead Components* and Paragraph 8.1.1 to read as follows: "Cast duplex (austenitic-ferritic) stainless steel UNS J93345 is acceptable in the solution-treated condition provided that the hardness does not exceed 223 HB. The material must be restricted to the following products: valve components, compressor components, casing and tubing heads (excluding mandrel hangers), spools, side entry caps, tail pieces, hammer caps, and spider caps. Laboratory tests have shown that duplex stainless steels' susceptibility to sulfide stress cracking is a function of the percentage of ferrite. The user may determine the acceptability of a duplex stainless steel with a given ferrite content for each application." *(Footnote) Aging over 500 F may reduce low-temperature toughness and reduce resistance to environmental cracking. ■