technical monograph 34

Sulfide Stress Cracking and the Commercial Application of NACE MR0175-84

Mark Adams
Senior Product Manager

James L. Gossett
Technical Consultant, Materials

FISHER®

FISHER-ROSEMOUNT™ Managing The Process Better.™

Fisher Controls

Sulfide Stress Cracking and the Commercial Application of NACE MR0175-84

Mark Adams
Senior Product Manager

James L. Gossett
Technical Consultant, Materials

The NACE Standard MR0175, "Sulfide Stress Corrosion Cracking Resistant Metallic Materials for Oil Field Equipment" is widely used throughout the world. The standard specifies the proper materials, heat treat conditions and strength levels required to provide good service life in sour gas and oil environments. NACE International (formerly the National Association of Corrosion Engineers) is a worldwide technical organization which studies various aspects of corrosion and the damage that may result in refineries, chemical plants, water systems and other types of industrial equipment.

MR0175 was first issued in 1975, but the origin of the document dates to 1959 when a group of engineers in Western Canada pooled their experience in successful handling of sour gas. The group organized as NACE committee T-1B and in 1963 issued specification 1B163, "Recommendations of Materials for Sour Service." In 1965, NACE organized the nationwide committee T-1F-1 which issued 1F166 in 1966 and MR0175 in 1975. The specification is now revised on an annual basis.

NACE committee T-1F-1 continues to have responsibility for MR0175. All revisions and additions must be unanimously approved by the 500 plus member committee T-1, Corrosion Control in Petroleum Production. MR0175 is intended to apply only to oil field equipment, flow line equipment and oil field processing facilities where H_2S is present. Only sulfide stress cracking (SSC) is addressed. Users are advised that other forms of failure mechanisms must be considered in all cases. Failure modes, such as severe general corrosion, chloride stress corrosion cracking, hydrogen blistering or step-wise cracking are outside the scope of the document. Users must carefully consider the process conditions when selecting materials.

While the standard is clearly intended to be used only for oil field equipment, industry has taken MR0175 and applied it to many other areas including refineries, LNG plants, pipelines and natural gas systems. The judicious use of the document in these applications is constructive and can help prevent SSC failures wherever H_2S is present.

The various sections of MR0175 cover the commonly available forms of materials and alloy systems. The requirements for heat treatment, hardness levels, conditions of mechanical work and post-weld heat treatment are addressed for each form of material. Fabrication techniques, bolting, platings and coatings are also addressed.

Figures 1 and 2 taken from MR0175 define the sour systems where SSC may occur. Low concentrations of H_2S at low pressures are considered outside the scope of the document. The low stress levels at low pressures or the inhibitive effects of oil may give satisfactory performance with standard commercial equipment. Many users, however, have elected to take a conservative approach and specify NACE compliance any time a measurable amount of H_2S is present.

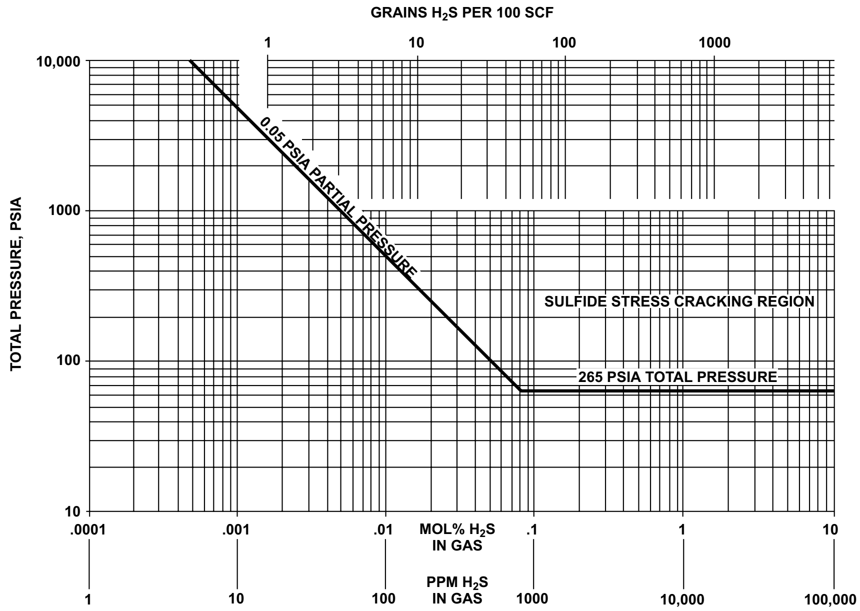

Fig. 1: Sour gas systems (see Paragraph 1.3.1).

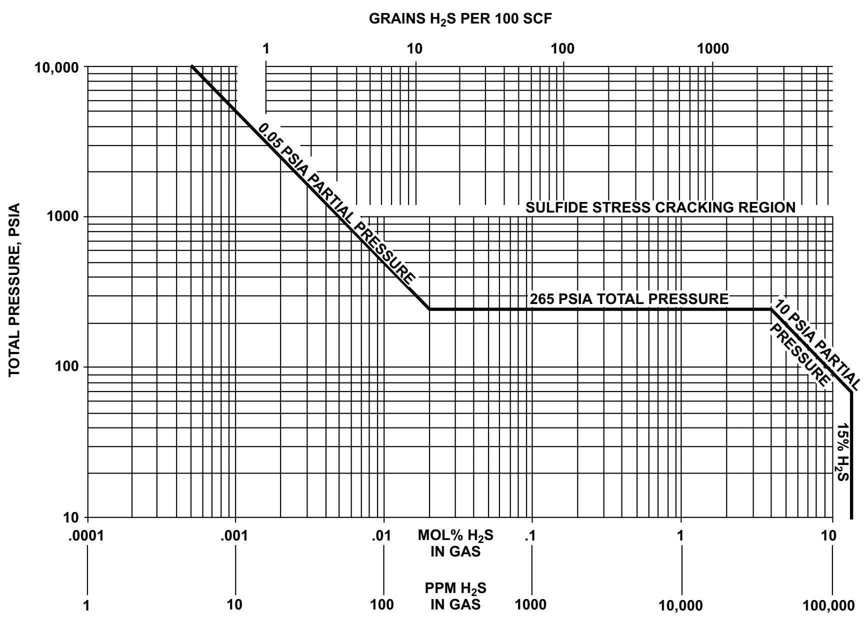

Fig. 2: Sour multiphase systems (see Paragraph 1.3.2).

The decision to follow MR0175 must be made by the user based on economic impact, the safety aspects should a failure occur and past field experience. Legislation can impact the decision as well. MR0175 must now be followed by law for sour applications under several jurisdictions; Texas (Railroad Commission), off-shore (under U.S. Minerals Management Service) and Alberta, Canada (Energy Conservation Board).

The Basics of Sulfide Stress Cracking

SSC develops in aqueous solutions as corrosion takes place on the surface of a material. Hydrogen ions are a product of many corrosion processes (Figure 3). These ions pick up electrons from the base material producing hydrogen atoms. At that point, two hydrogen atoms may combine to form a hydrogen molecule. Most molecules will eventually collect, form hydrogen bubbles and float away harmlessly. However, some percentage of the hydrogen atoms will diffuse into the base metal and embrittle the crystalline structure. When a certain critical concentration of hydrogen is reached and combined with a tensile stress exceeding a threshold level, SSC will occur. H_2S does not actively participate in the SSC reaction; however, sulfides act to promote the entry of the hydrogen atoms into the base material.

In many instances, particularly among carbon and low alloy steels, the cracking will initiate and propagate along the grain boundaries. This is called intergranular stress cracking. In other alloy systems or under certain specific conditions, the cracking will propagate through the grains. This is called transgranular stress corrosion cracking.

Sulfide stress cracking is most severe at ambient temperature, particularly in the range of 20 to 120°F (-7 to 49°C). Below 20°F (-7°C) the diffusion rate of the hydrogen is so slow that the critical concentration is never reached. Above 120°F (49°C) the diffusion rate is so fast that the hydrogen passes through the material in such a rapid manner that again the critical concentration is not reached. The occurrence of stress corrosion cracking above 120°F (49°C), however, is still very likely and must be very carefully considered when selecting materials. In most cases, however, the stress corrosion cracking will not be SSC but some other form. Chloride stress corrosion cracking is likely in deep sour wells as most exceed 300°F (149°C) and contain significant chloride levels.

The susceptibility of a given type of material to SSC is directly related to its strength or hardness level. This is true for carbon steels, stainless steels and nickel base alloys. As an example, when carbon or alloy steel is heat treated to progressively higher hardness levels, the time to failure decreases rapidly for a given stress level (See Figure 4). Years of field experience have shown that good SSC resistance is obtained below 22 HRC for the carbon and low alloy steels. SSC can still occur below 22 HRC, but the likelihood of failure is greatly reduced.

Carbon Steel

Carbon and low alloy steels have acceptable resistance to SSC provided their processing is very carefully monitored. The hardnesses must be less than 22 HRC. If welding or significant cold working is done, stress relief is required. Even though the base metal hardness of a carbon or alloy steel is less than 22 HRC, areas of the heat effected zone will be harder. Post-weld heat treatment will eliminate these excessively hard areas.

ASME SA216 grades WCB and WCC and ASME SA105 are the most commonly used body materials. It is Fisher's policy to stress relieve all welded carbon steels that are supplied to MR0175.

ASME SA352 grades LCB and LCC are very similar to WCB and WCC. They are impact tested at -50°F (-46°C) to insure good toughness in low temperature service. LCB and LCC are used in the northern U.S., Alaska and Canada where temperatures commonly drop below the -20°F (-32°C) permitted for WCB. All welded LCB and LCC castings to MR0175 are also stress relieved.

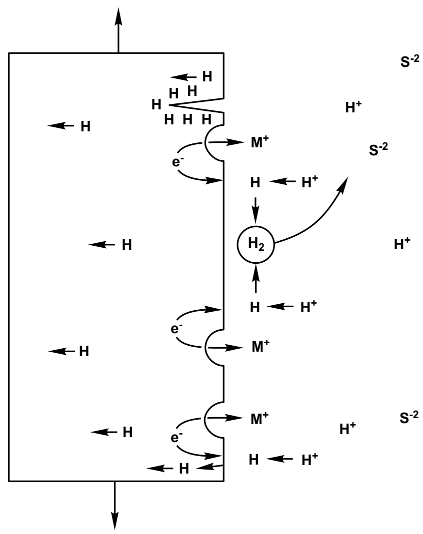

Fig. 3: Schematic showing the generation on entry of hydrogen producing SSC.

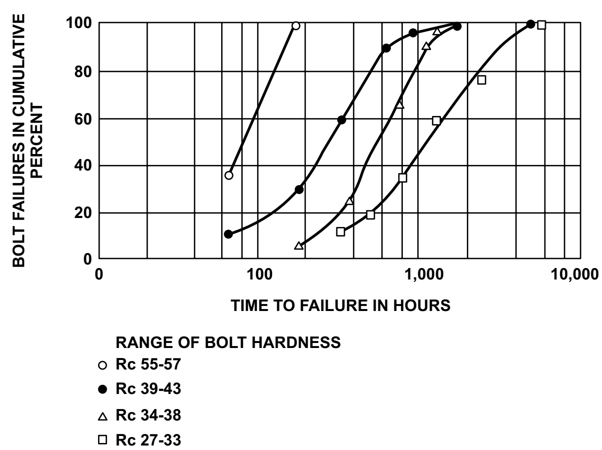

Fig. 4: Effect of hardness on time to failure of AISI 4140 steel bolts in H_2S + water at 104°F and 250 PSI

Cast Iron

Gray, austenitic and white cast irons cannot be used for any pressure retaining parts, due to low ductility. Ferritic ductile iron to ASTM A395 is acceptable when permitted by ANSI, API or other industry standards.

Stainless Steel

UNS S41000 (410 stainless steel SST) and other martensitic grades must be double tempered to a maximum allowable hardness level of 25 HRC. Post-weld heat treatment is also required. S41600 (416 SST) is similar to S41000 (410) with the exception of a sulfur addition to produce free machining characteristics. Use of free machining steels is not permitted by MR0175.

CA6NM is a modified version of the cast S41000 stainless steel. MR0175 allows its use, but specifies the exact heat treatment required. Generally, the carbon content must be restricted to 0.3% maximum to meet the 23 HRC maximum hardness. Post-weld heat treatment is required for CA6NM.

The austenitic stainless steels have exceptional resistance to SCC in the annealed condition. The standard specifies that these materials must be 22 HRC maximum and free of cold work to prevent SSC. The cast and wrought equivalents of 302, 304, 304L, 305, 308, 309, 310, 316, 316L, 317, 321, 347 and N08020 (alloy 20) are all acceptable per MR0175.

Post-weld heat treatment of the 300 Series SST is not required. The corrosion resistance may be affected by welding. However, this can be controlled by using the low carbon grades, or low heat input levels and low interpass temperatures.

Wrought S17400 (17-4PH) stainless steel is allowed, but must be carefully processed to prevent SSC. The standard now gives two different acceptable heat treatments for S17400. One treatment is the double H1150 heat treatment which requires exposing the material at 1150°F (621°C) for four hours followed by air cooling and then exposing for another four hours at 1150°F (621°C). A maximum hardness level of 33 HRC is specified. The second heat treatment is the H1150M treatment. First, the material is exposed to two hours at 1400°F (760°C), then air cooled and exposed for four hours at 1150°F (621°C). The maximum hardness level is the same for this condition.

CB7Cu-1 (Cast 17-4PH) in the double H1150 condition is approved per MR0175 for internal valve and regulator components. Many users have successfully applied it for trim parts in past years.

Two high strength stainless steel grades are acceptable for MR0175. The first is S66286 (grade 660 or A286) which is a precipitation hardening alloy with excellent resistance to SSC and general corrosion. The maximum hardness level permitted is 35 HRC.

The second material is S20910 (XM-19) which is commonly called Nitronic 50®. This high strength SST has excellent resistance to SSC and corrosion resistance superior to S31600 or S31700. The maximum allowable hardness is 35 HRC. The "high strength" condition, which approaches 35 HRC, can only be produced by hot working methods. Cold drawn S20910 is also acceptable for shafts, stems and pins. It is our experience that the SSC resistance of S20910 is far superior to S17400 or other austenitic stainless steels at similar hardness levels. The only other materials with similar stress cracking resistance at these strength levels are the nickel-based alloys which are, of course, much more expensive.

A few duplex stainless steels are now acceptable per MR0175. Wrought S31803 (2205) and S32550 (Ferralium 255®) are both acceptable to 28 HRC. Wrought S32404 (Uranus 50®) is acceptable to 20 HRC. Only one cast duplex SST is acceptable for unrestricted application, alloy Z 6CNDU20.08M, NF A 320-55 French National Standard. Fisher has supplied valves cast in this material.

Other duplex stainless steels are also acceptable, however, there are several environmental restrictions. Wrought duplex stainless steel UNS S32760 (Zeron 100®) is acceptable in the solution-annealed and cold-worked condition at a maximum hardness of 34 HRC. The cast version UNS J93380 (or CD3MWCuN) is acceptable in the solution-annealed and quenched condition at a maximum hardness of 24 HRC. Both are restricted for use in sour environments containing up to 120,000 mg/l chloride ion if the partial pressure of H_2S does not exceed 0.020 MPa (3.0 psi). If the chloride ion concentration is always less than 15,000 mg/l and the pH of the aqueous phase is always greater than 5.6, then this material condition is acceptable if the partial pressure of H2S does not exceed 0.10 MPa (15 psi)

Nonferrous Alloys

The final category in MR0175 is the nonferrous materials section. In general, the nickel-base alloys are acceptable to a maximum hardness level of 35 HRC. All have excellent resistance to SSC. Commonly used acceptable materials include nickel-copper alloys N04400 (alloy 400), M35-1 and M35-2 (cast alloy 400) and N04405 (alloy 405) and the precipitation hardening alloy N05500 (K500). The nickel-iron-chromium alloys include alloys N06600 (alloy 600) and N07750 (alloy X750). The acceptable nickel-chromium-molybdenum alloys include alloys N06625 (alloy 625), N10276 (alloy C276) and CW2M (Fisher's standard cast alloy C). The precipitation hardening grade N07718 (alloy 718) is also acceptable to 40 HRC. Where high strength levels are required along with good machinability, Fisher uses N05500, N07718, N07750 or N07725 (alloy 725). They can be drilled or turned, then age hardened. Several cobalt base materials are acceptable, including R30035 (alloy MP35N), R30003 (Elgiloy®) and R30605 (Haynes 25® or L605).

Aluminum base and copper alloys may be used for sour service, but the user is cautioned that severe corrosion attack may occur on these materials. They are seldom used in direct contact with H^2S.

Several wrought titanium grades are now included in MR0175. The only common industrial alloy is wrought R50400 (grade 2). Cast titanium is not included in MR0175.

Springs

Springs in compliance with NACE represent a difficult problem. To function properly, springs must have very high strength (hardness) levels. Normal steel and stainless steel springs would be very susceptible to SSC and fail to meet MR0175.

In general, very soft, low strength materials must be used. Of course, these materials produce poor springs. The two exceptions allowed are the cobalt based alloys, such as R30003, which may be cold worked and hardened to a maximum hardness of 60 HRC and alloy N07750 which is permitted to 50 HRC.

Coatings

Coatings, platings and overlays may be used provided the base metal is in a condition which is acceptable per MR0175. The coatings may not be used to protect a base material which is susceptible to SSC. Coatings commonly used in sour service are chromium plating, electroless nickel (ENC) and nitriding. Overlays and castings commonly used include CoCr-A (Stellite® or alloy 6), R30006 (alloy 6B), and NiCr-C (Colmonoy® 6) nickel-chromium-boron alloys. Tungsten carbide alloys are acceptable in the cast, cemented or thermally sprayed conditions. Ceramic coatings such as plasma sprayed chromium oxide are also acceptable.

ENC is often used by Fisher as a wear resistant coating. As required by MR0175, it is applied only to acceptable base metals. ENC has excellent corrosion resistance in sour, salt containing environments.

Stress Relieving

Many people have the misunderstanding that stress relieving following machining is required by MR0175. Provided good machining practices are followed using sharp tools and proper lubrication, the amount of cold work produced is negligible. SSC resistance will not be affected.

MR0175 actually permits the cold rolling of threads, provided the component will meet the heat treat conditions and hardness requirements specified for the given parent material. Cold deformation processes such as burnishing are also acceptable.

Bolting

Bolting materials must meet the requirements of MR0175 when bolting is directly exposed to a sour environment. Standard ASTM A193 grade B7 bolts or A194 grade 2H nuts can be used per MR0175 provided they are outside of the sour environment. If the bolting will be deprived atmospheric contact by burial, insulation or flange protectors, then grades of bolting such as B7 and 2H are unacceptable. The most commonly used fasteners for "exposed" applications are ASTM A193 grade B7M bolts and A194 grade 2M nuts. They are tempered and hardness tested versions of the B7 and 2H grades. HRC 22 is the maximum allowable hardness.

Many customers use only B7M bolting for bonnet, packing box, and flange joints. This reduces the likelihood of SSC if a leak develops and goes undetected or unrepaired for an extended time. It must be remembered, however, that use of lower strength bolting materials such as B7M often requires pressure vessel derating. Fisher offers special S17400 double H1150 bolting at the full B7 rating to overcome the derating problem.

Bolting Coatings

ENC coating is acceptable on pressure-retaining and non-pressure-retaining fasteners.

For some reason, there is often confusion regarding the acceptability of zinc plated fasteners per NACE MR0175. NACE MR0175 does not preclude the use of any coating, provided it is not used in an attempt to prevent sulfide stress cracking of an otherwise unacceptable base material. However, zinc plating of pressure-retaining bolting is not recommended by Fisher Controls due to metal-induced embrittlement concerns.

Composition Materials

MR0175 does not address elastomer and polymer materials. However, the importance of these materials in critical sealing functions cannot be over-looked. User experience has been successful with elastomers such as nitrile, neoprene and the fluoro- and perfluoroelastomers. In general, fluoropolymers such as TFE can be applied without reservation within their normal temperature range.

Codes and Standards

Applicable ASTM, ANSI, ASME and API standards are used along with MR0175 as they would normally be used for other applications. The MR0175 requires that all weld procedures be qualified to these same standards. Welders must be familiar with the procedures and capable of making welds which comply.

The Commercial Application of NACE

Special documentation of materials to MR0175 is not required by the standard and NACE itself does not issue any type of a certification. It is the producers responsibility to properly monitor the materials and processes as required by MR0175.

It is not uncommon for manufacturers to "upgrade" standard manufactured components to MR0175 by hardness testing. This produces a product which complies with MR0175, but which may not provide the best solution for the long-term. If the construction was not thoroughly recorded at the outset, it may be difficult to get spare parts in the proper materials. The testing necessary to establish that each part complies is quite expensive. And, due to the "local" nature of a hardness test, there is also some risk that "upgraded" parts do not fully comply.

With proper in-house systems, it is quite simple to confidently produce a construction which can be certified to MR0175 without the necessity of after manufacture testing. This eliminates many cost extras and additionally provides a complete record of the construction for future parts procurement. An order entry, procurement and manufacturing system which is integrated and highly structured is required in order to confidently and automatically provide equipment which complies.

Due to its hierarchical nature and its use by all company functions, the Fisher system is ideal for items such as MR0175 which requires a moderate degree of control without undue cost. In order to illustrate the system used by Fisher, an example will be used.

Most products produced by Fisher (including products to MR0175) will be specified by a Fisher Standard (FS) number. These numbers (e.g. FSED-542) completely specify a standardized construction including size, materials and other characteristics. The FS number is a short notation which represents a series of part groups (modules) describing the construction. One module may represent, for instance, a 3" WCC valve body with ANSI Class 300 flanges, another may specify a certain valve plug and seat ring. The part numbers which make up these modules are composed of a drawing number and a material/finish identifier. The drawing describes the dimensions and methods used to make the part while the material/finish reference considers material chemistry, form, heat treatment and a variety of other variables. The part number definition also includes a very specific "material reference number" which is used to identify a material specification for purchase of materials. The material specification includes the ASME designation as well as additional qualifiers as necessary to assure compliance with specifications such as NACE MR0175 (see Figure 5).

For NACE compliant products an FS number and a NACE option are generally specified. The FS number establishes the standard construction variation. The option modifies the construction and materials to comply totally with MR0175 requirements. The option eliminates certain standard modules and replaces them with NACE suitable modules. Each part in a NACE suitable module has been checked to assure that it complies to the specification in form and manufacturing method and that it is produced from an appropriate material.

It is due to this top to bottom system integrity that Fisher can be confident of MR0175 compliance without the need for extensive test work. At each level of the system documentation, there are specific references to and requirements for compliance to MR0175. Further, since the construction is permanently documented at all levels of detail, it is possible to confidently and simply procure spare parts at any future date.

Test documentation is available in a variety of forms, including certificates of compliance, hardness test data, chemical and physical test reports and heat treat reports. Since these items will have some cost associated with them, it is important to examine the need for documentation in light of the vendors credibility and his manufacturing control systems. Fisher's normal manufacturing processes and procedures assure that all NACE specified products will comply without the need for additional test expense.

Fisher has been producing equipment for a variety of sour conditions and specifications since the mid-1950's and have thousands of devices in service. MR0175 has been shown to be an excellent technical reference for solving the complex application problems found in the handling of sour fluids. As more sour hydrocarbons are produced, it grows in importance and applicability.

UNS Numbers	Material Designation or Tradename	UNS Numbers	Material Designation or Tradename
AWS 5.13	CoCr-A	N09925	Incoloy 925
	Stellite 6		Alloy 925
	Alloy 6		
		N10002	Hastelloy C
AWS 5.13	NiCr-C		Alloy C
	Colmonoy 6		CW12MW
			CW2M
British Standard Aerospace	Nimonic 105		
Series HR3		N10276	Hastelloy C276
K66286	A-286	R05200	Commercially Pure
(now S66286)	Grade 660		Tantalum
N04400	Monel 400	R30003	Elgiloy
	Alloy 400		
	M35-1	R30004	Havar
	M35-2		
		R30035	MP35N
N04405	Monel R405		
	R Monel	R30260	Duratherm 2602
	Alloy R405		
		R30605	L605
N05500	Monel K500		Haynes Alloy 25
	K Monel		
	K500	R50400	Titanium Grade 2
			RMI 40
N06002	Hastelloy X		Ti-50A
	Pyromet Alloy 680		ALSMet Gr 2
			Cabot Ti-40
N06007	Hastelloy G		
		R53400	Grade 12
N06110	Allcorr		Ti Code-12
N06600	Inconel 600	R56260	RMI 6A1-2Sn-4Zr-6Mo
	Alloy 600		Alpha-Beta
	CY40		
		R58640	Beta Ti
N06625	Inconel 625		Ti-38-6-44
	Alloy 625		Ti-3A1-8V-6Cr-4Zr-4Mo
	CW6MC		
		S15700	PH15-7Mo
N06985	Hastelloy G-3		15-7Mo
N07031	Pyromet 31	S20910	Nitronic 50
			22Cr-13Ni-5MN
N07718	Inconel 718		ASTM Grade XM19
	Alloy 718		
	Pyrotool 7	S17400	17-4PH
			Custom 630
N07750	Inconel X750		
	Alloy X750	S45000	Custom 450
N08020	Carpenter 20Cb-3	S20910	Nitronic 50
	Alloy 20	ASTM Grade XM19	22Cr-13Ni-5MN
	Duromet 20		
	CN7M	S31803	SAF2205
		DIN 1.4462	2205
N08028	Sanicro 28		
		S32550	Ferralium Alloy 255
N08800	Incoloy 800		
	Alloy 800	S45000	Custom 450
N08825	Incoloy 825	Z6CNDU20.08M	Uranus 50M
	Alloy 825		

Fisher Controls	Material Specification	No. FMS 20B31	E
		By LLW	9-8-81
FISHER	GRADE CA-6NM to NACE MR-01-75	Apvd TKB	9-10-81
		Page 1	of 1
©Fisher Controls 1982, 1985		Rev JLG	10-22-85

1. SCOPE

This specification covers Grade CA-6NM with a controlled chemistry range to meet NACE MR-01-75.

2. MATERIAL REFERENCE NUMBER

(a) ASME SA-487-334M
(b) ASME SA-352-335W

3. REQUIREMENTS

All castings supplied to this specification shall meet all requirements of ASME SA-487 or SA-352 as specified and the following additional requirements:

3.1 Carbon content 0.03% maximum to meet HRC 23 maximum.

3.2 Austenitize at 1850°F minimum, air cool or oil quench at room temperature.

3.3 Temper at 1250°F, air cool.

3.4 Temper at 1125°F, air cool.

4. POST WELD HEAT TREATMENT

All castings must be post-weld heat treated (PWHT) per 3.3 and 3.4. If all foundry weld repairs are made prior to the quench and temper treatment, no additional treatment will be required.

5. HARDNESS

The hardness of each casting shall be HRC 23 max. Where conversion to Brinell is required, the equivalent to HRC 23 shall be determined on a separate test bar poured with each heat. The test bar shall be heat treated along with the castings.

FMS3-8/1

Form FC3911/Printed in U.S.A.

Fig. 5: Fisher material purchase specification citing compliance to NACE MR0175 in addition to other standard parameters.

Fisher Controls International, Inc.
205 South Center Street
Marshalltown, Iowa 50158
Phone: (641) 754-3011
Fax: (641) 754-2830
Email: fc-valve@frmail.frco.com
Website: www.fisher.com

D350412X012 / Printed in the U.S.A./8-99

FISHER-ROSEMOUNT™ Managing The Process Better.™