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Petroleum, petrochemical and natural gas industries — Metallic materials resistant to sulfide stress cracking in corrosive petroleum refining environments

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National foreword

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The UK participation in its preparation was entrusted to Technical Committee PSE/17, Materials and equipment for petroleum, petrochemical and natural gas industries.

A list of organizations represented on this committee can be obtained on request to its secretary.

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Petroleum, petrochemical and natural gas industries - Metallic materials resistant to sulfide stress cracking in corrosive petroleum refining environments (ISO 17945:2015)

Industries du pétrole, de la pétrochimie et du gaz naturel - Matériaux métalliques résistant à la fissuration sous contrainte induite par les sulfures pour utilisation dans des environnements corrosifs de raffinage du pétrole (ISO 17945:2015)

Erdöl-, petrochemische und Erdgasindustrie - Metallische Werkstoffe beständig gegen Schwefelwasserstoff-Rissbildung in korrosiver Erdölraffinerieumgebung (ISO 17945:2015)

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Foreword

This document (EN ISO 17945:2015) has been prepared by Technical Committee ISO/TC 67 “Materials, equipment and offshore structures for petroleum, petrochemical and natural gas industries” in collaboration with Technical Committee CEN/TC 12 “Materials, equipment and offshore structures for petroleum, petrochemical and natural gas industries” the secretariat of which is held by AFNOR.

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Foreword

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Introduction

The term “wet H_2S cracking”, as used in the refining industry, covers a range of damage mechanisms that can occur because of the effects of hydrogen charging in wet H_2S refinery or gas plant process environments. One of the types of material damage that can occur as a result of hydrogen charging is sulfide stress cracking (SSC) of hard weldments and microstructures, which is addressed by this International Standard. Other types of material damage include hydrogen blistering, hydrogen-induced cracking (HIC), and stress-oriented hydrogen-induced cracking (SOHIC), which are not addressed by this International Standard.

Historically, many end users, industry organizations (e.g. API), and manufacturers that have specified and supplied equipment and products such as rotating equipment and valves to the refining industry have used NACE MR0175/ISO 15156 to establish materials requirements to prevent SSC. However, it has always been recognized that refining environments are outside the scope of NACE MR0175/ISO 15156, which was developed specifically for the oil and gas production industry. In 2003, the first edition of NACE MR0103 was published as a refinery-specific sour service metallic materials standard. This International Standard is based on the good experience gained with NACE MR0175/ISO 15156, but tailored to refinery environments and applications. Other references for this International Standard are NACE SP0296, NACE Publication 8X194, NACE Publication 8X294, and the refining experience of the task group members who developed NACE MR0103.

The materials, heat treatments, and material property requirements set forth in NACE MR0103 are based on extensive experience in the oil and gas production industry, as documented in NACE MR0175/ISO 15156, and were deemed relevant to the refining industry by the task group.

This International Standard was developed on the basis of NACE MR0103.

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INTERNATIONAL STANDARD ISO 17945:2015(E)

Petroleum, petrochemical and natural gas industries — Metallic materials resistant to sulfide stress cracking in corrosive petroleum refining environments

1 Scope

This International Standard establishes material requirements for resistance to SSC in sour petroleum refining and related processing environments containing H_2S either as a gas or dissolved in an aqueous (liquid water) phase with or without the presence of hydrocarbon. This International Standard does not include and is not intended to include design specifications. Other forms of wet H_2S cracking, environmental cracking, corrosion, and other modes of failure are outside the scope of this International Standard. It is intended to be used by refiners, equipment manufacturers, engineering contractors, and construction contractors.

Specifically, this International Standard is directed at the prevention of SSC of equipment (including pressure vessels, heat exchangers, piping, valve bodies, and pump and compressor cases) and components used in the refining industry. Prevention of SSC in carbon steel categorized under P-No. 1 in Section IX of the ASME Boiler and Pressure Vessel Code (BPVC) is addressed by requiring compliance with NACE SP0472.

This International Standard applies to all components of equipment exposed to sour refinery environments (see Clause 6) where failure by SSC would (1) compromise the integrity of the pressure-containment system, (2) prevent the basic function of the equipment, and/or (3) prevent the equipment from being restored to an operating condition while continuing to contain pressure.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

NACE Standard TM0177, *Laboratory Testing of Metals for Resistance to Sulfide Stress Cracking and Stress Corrosion Cracking in H2S Environments*[1)]

ANSI/NACE MR0175/ISO 15156, *Petroleum and natural gas industries — Materials for use in H2S-containing environments in oil and gas production*[1)]

ASTM A833, *Standard Practice for Indentation Hardness of Metallic Materials by Comparison Hardness Testers*

ASTM E384, *Standard Test Method for Knoop and Vickers Hardness of Materials*

ASTM E562, *Standard Test Method for Determining Volume Fraction by Systematic Manual Point Count*

SAE AMS2430, *Shot Peening, Automatic*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
lower transformation temperature
A_{c1}
temperature at which austenite begins to form during heating

1) NACE International, 1440 South Creek Dr., Houston, TX 77084-4906, USA.

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3.2
upper transformation temperature
A_{c3}
temperature at which transformation of ferrite to austenite is completed during heating

3.3
alloy steel
iron-based alloy containing carbon (usually less than 2,5 %) and manganese (usually not less than 0,25 %), that contains specified minimum quantities for one or more alloying elements other than manganese, silicon, and copper, and that does not specify a minimum chromium content greater than or equal to 10 %

3.4
austenitic stainless steel
stainless steel whose microstructure, at room temperature, consists predominantly of austenite

3.5
carbon steel
iron-based alloy containing carbon (usually less than 2,0 %) and manganese (usually not less than 0,25 %), with no specified minimum quantity for any alloying element other than manganese, silicon, and copper, and that contains only an incidental amount of any element other than carbon, silicon, manganese, copper, sulfur, and phosphorus

3.6
cladding
metallurgically bonded layer (roll bonded, explosion bonded, or weld overlaid) of a corrosion-resistant alloy material applied to the entire wetted surface of a substrate material that is relatively less corrosion-resistant

Note 1 to entry: See also weld overlay.

3.7
duplex stainless steel
austenitic/ferritic stainless steel
stainless steel whose microstructure at room temperature consists primarily of a mixture of austenite and ferrite

3.8
end user
company or agency that owns and operates the component (e.g. vessel, piping, pump, compressor, etc.)

3.9
ferritic stainless steel
stainless steel whose microstructure, at room temperature, consists predominantly of ferrite

3.10
stainless steel
iron-based alloy containing 10,5 % mass fraction or more chromium, possibly with other elements added to secure special properties

3.11
sulfide stress cracking
SSC
cracking of a metal under the combined action of tensile stress and corrosion in the presence of water and H_2S (a form of hydrogen stress cracking)

3.12
thermal spray coating
high-temperature process by which finely divided metallic or nonmetallic materials are deposited in a molten or semi-molten condition to form a coating on a surface when cooled

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3.13
weld overlay, corrosion resistant
deposition of one or more layers of corrosion resistant weld metal to the surface of a base material in an effort to improve the corrosion resistance properties of the surface

Note 1 to entry: See also cladding.

3.14
weld overlay, hard facing
deposition of one or more layers of a weld metal to the surface of a material in an effort to improve the wear resistance properties of the surface

4 Symbols and abbreviated terms

ANSI	American National Standards Institute
API	American Petroleum Institute
ASME	ASME (formerly American Society of Mechanical Engineers)
AWS	American Welding Society
BPVC	boiler and pressure vessel code
HAZ	heat-affected zone
HI	heat input
HIC	hydrogen-induced cracking
NACE	NACE International (formerly National Association of Corrosion Engineers)
ppmw	parts per million by weight, commonly expressed as mg/kg in SI units
PQR	procedure qualification record
PREN	pitting resistance equivalent number
PWHT	postweld heat treatment
SOHIC	stress-oriented hydrogen-induced cracking
SSC	sulfide stress cracking
UNS	unified numbering system (for metals and alloys)
WPQT	welding procedure qualification test

5 Responsibilities

5.1 Responsibilities of the end user

5.1.1 It is the responsibility of the end user (or the end user's agent) to determine the operating conditions and to specify when this International Standard applies.

5.1.2 It is the end user's (or the end user's agent's) responsibility to ensure that a material is satisfactory in the intended environment. The end user (or the end user's agent) may select specific materials for use on the basis of operating conditions that include pressure, temperature, corrosiveness, and fluid

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properties. A variety of candidate materials may be selected from this International Standard for any given component. Unlisted materials may also be used based on either of the following processes.

a) If a metallurgical review based on scientific and/or empirical knowledge indicates that the SSC resistance will be adequate, these materials may then be proposed for inclusion into the standard using methods in Clause 9.

b) If a risk-based analysis indicates that the occurrence of SSC is acceptable in the subject application.

5.1.3 Other forms of wet H_2S cracking, environmental cracking, corrosion, and other modes of failure, although outside the scope of this International Standard, should be considered in the design and operation of equipment. Severely corrosive and/or hydrogen charging conditions may lead to failures by mechanisms other than SSC and should be mitigated by methods that are outside the scope of this International Standard.

5.2 Responsibility of the manufacturer

The manufacturer is responsible for meeting the metallurgical requirements of this International Standard.

6 Factors contributing to SSC

6.1 General parameters affecting SSC

SSC in refining equipment is affected by complex interactions of parameters including the following:

a) chemical composition, strength (as indicated by hardness), heat treatment, and microstructure of the material exposed to the sour environment;

b) total tensile stress present in the material (applied plus residual);

c) hydrogen flux generated in the material, which is a function of the environment (i.e. presence of an aqueous phase, H_2S concentration, pH, and other environmental parameters such as bisulfide ion concentration and presence of free cyanides);

d) temperature;

e) time.

6.2 Effect of material condition and stress level on susceptibility to SSC

6.2.1 Material susceptibility to SSC is primarily related to material strength (as indicated by hardness), which is affected by chemical composition, heat treatment, and microstructure. Materials with high hardness generally have an increased susceptibility to SSC.

6.2.2 SSC has not generally been a concern for carbon steels typically used for refinery pressure vessels and piping in wet H_2S service because these steels have sufficiently low hardness levels.

6.2.3 Improperly heat-treated metals, weld deposits, and heat-affected zones (HAZ), however, may contain regions of high hardness.

6.2.4 Susceptibility for a given material increases with increased tensile stress.

6.2.5 Residual stresses contribute to the overall tensile stress level. High residual stresses associated with welds increase susceptibility to SSC.

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6.2.6 Control of weldment hardness, with or without reduction of residual stresses, is a recognized method for preventing SSC, as outlined in NACE SP0472 for P-No. 1 carbon steels.

6.3 Effect of hydrogen permeation flux on SSC

6.3.1 Susceptibility to SSC is also related to the hydrogen permeation flux in the steel, which is primarily associated with two environmental parameters: pH and total sulfide content of the aqueous phase. In a closed system at equilibrium condition, dissolved hydrogen sulfide (H_2S_{aq}), bisulfide ion (HS^-), and sulfide ion (S^{2-}) (sometimes called "soluble sulfide") exist in an aqueous solution in different pH ranges.

6.3.2 The sulfide species plot exhibited in Figure A.1 shows their relative amounts present in an aqueous solution at 25 C (77°F) as a function of pH. At pH less than 6, H_2S_{aq} is the dominant (>90 % of total) sulfide specie present in the aqueous phase. At pH between 8 and 11, the dominant (>90 % of total) sulfide specie present in the aqueous phase is HS^-. At pH greater than 13, the dominant (>90 % of total) sulfide specie present in the aqueous phase is S^{2-}. At pH 7, the system contains 50 % H_2S_{aq}, 50 % HS^-, and virtually no S^{2-}. At pH 12, the system contains 50 % HS^-, 50 % S^{2-}, and virtually no H_2S_{aq}. The total sulfide content, therefore, refers to the total amount of all three sulfide species present in the aqueous phase (i.e. the sum of H_2S_{aq}, HS^-, and S^{2-}).

6.3.3 Typically, the hydrogen flux in steels has been found to be lowest in near-neutral pH solutions, with increasing flux at both lower and higher pH values. Corrosion at lower pH values is typically caused by H_2S_{aq}, whereas corrosion at higher pH values is typically caused by high concentrations of HS^-.

6.3.4 In many refinery sour water environments, the presence of dissolved ammonia (NH_3) increases the pH, thereby increasing the solubility of H_2S and resulting in a high HS^- concentration. At elevated pH, the presence of free cyanides, which include dissolved hydrogen cyanide (HCN_{aq}) and cyanide ion (CN^-), can further aggravate the degree of atomic hydrogen charging into the steel. Even though SSC susceptibility is known to increase with total sulfide content of the aqueous phase, the presence of as little as 1 ppmw total sulfide in the aqueous phase can cause SSC under conditions that promote aggressive hydrogen charging.

6.3.5 For carbon steel, some environmental conditions known to cause SSC are those containing an aqueous (liquid water) phase and either of the following:

a) >50 ppmw total sulfide content in the aqueous phase;

b) ≥1 ppmw total sulfide content in the aqueous phase and pH < 4;

c) ≥1 ppmw total sulfide content and ≥20 ppmw free cyanide in the aqueous phase, and pH > 7,6;

d) >0,3 kPa absolute (0,05 psia) partial pressure H_2S in the gas phase associated with the aqueous phase of a process.

6.3.6 The high-pH sour environments differentiate refinery sour service from the oil and gas production sour environments covered by NACE MR0175/ISO 15156, because many wet sour streams in oil and gas production also contain carbon dioxide and, hence, exhibit a lower pH. Another major difference is that chloride ion concentrations tend to be significantly lower in refinery sour services than in oil production sour services.

6.4 Effect of elevated temperature exposure on SSC

The hydrogen charging potential increases with increasing temperature provided the aqueous phase is not eliminated by the elevated temperature. Elevated temperature promotes dissociation of H_2S (thereby producing more monatomic hydrogen), and increases the diffusion rates of monatomic hydrogen in metals, thereby promoting hydrogen charging. However, cracking potential is maximized at near-ambient temperature. This distinction is important because metals can become charged during

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high-temperature exposure and subsequently crack during excursions to lower temperatures (such as during shutdowns).

6.5 Factors affecting time to failure due to SSC

The time to failure decreases as material strength, total tensile stress, and environmental charging potential increase. Exposure time to cause SSC can be very short, if the other SSC factors favour susceptibility. Some susceptible equipment can fail even during short sour water excursions such as those encountered during equipment shutdowns.

6.6 Bases for establishing whether equipment falls within the scope of this International Standard

The end user (or the end user's agent) shall determine whether the parameters necessary to cause SSC exist in the process environment, and whether the equipment falls within the scope of this International Standard. The end user (or the end user's agent) may rely on experience, risk-based analysis, or the above guidance (notably that related to environmental conditions provided in 6.3 and 6.4) to make this determination. When determining whether the equipment falls within the scope of this International Standard, consideration should be given to all plant operating scenarios and the likely impact on the materials of construction, i.e. normal operations, operational upsets, alternate (possible future) operations, and start-up/shutdown conditions (e.g. presulfiding of catalysts).

7 Materials included in this International Standard

7.1 Materials included in this International Standard are resistant to, but not necessarily immune to, SSC. Materials have been included based on their demonstrated resistance to SSC in field applications, in SSC laboratory testing, or both.

7.2 Listed materials do not all exhibit the same level of resistance to SSC. Standard laboratory SSC tests, such as those addressed in NACE Standard TM0177, are accelerated and severe tests. Materials that successfully pass these tests are generally more resistant to cracking in sour service than materials that fail the tests. Many alloys included in this International Standard perform satisfactorily in sour service even though they may crack in laboratory tests.

7.3 Improper design, processing, installation, or handling can cause resistant materials to become susceptible to SSC.

7.4 No effort has been made in this International Standard to rank materials based on their relative resistance to SSC. Selection of the appropriate material for a given application depends on a number of factors, including mechanical properties, corrosion resistance, and relative resistance to SSC, and is beyond the scope of this International Standard.

7.5 There are a number of instances where this International Standard specifically references the ASME BPVC. There are other instances where this International Standard references specific industry standards and/or designations for material grades, conditions, and testing requirements (e.g. ASTM, NACE, API, and UNS numbers). In these cases, the use of alternate "equivalent" standards, grade designations, condition designations, or testing methods shall only be permitted when approved by the end user. It is the responsibility of the agency requesting the substitution to provide to the end user sufficient information, data, etc. in order to prove "equivalency." If it is not clear that an alternate standard, grade designation, and/or condition designation is identical to the standard, grade designation, and/or condition designation specified in this International Standard, the end user is strongly advised to follow the requirements stipulated in Clause 11 to evaluate the acceptability of the alternate material.

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8 Hardness requirements

8.1 Hardness is related to tensile strength, a primary factor in SSC susceptibility. Because hardness testing is non-destructive and requires relatively minor component/specimen preparation compared with tensile testing, it is commonly used by manufacturers in production quality control and by users in field inspection. As such, a maximum allowable hardness is specified as a primary requirement for many of the materials in this International Standard.

8.2 Several different hardness scales are used in this International Standard. The most commonly used scales are Rockwell "C" (HRC), Rockwell "B" (HRBS), Brinell (HBW), and Vickers 49 N (5 kgf) or 98 N (10 kgf) (HV 5 or HV 10). Background information on these hardness scales and the logic behind the various references is provided in Annex B.

8.3 Hardness testing and reporting shall be performed in strict compliance with the methods described in the appropriate ASTM or ISO standards. Annex B lists the appropriate standards for the various test methods.

8.4 The standard test parameters (indenters, loads, and major-load dwell time) shall be used for all Rockwell hardness tests. The specimen temperature for Rockwell hardness testing shall be 10 °C to 35 °C (50 °F to 95 °F). No lubricant shall be used. Because Brinell hardness tests are only indicated for steel materials in this International Standard, all Brinell hardness tests shall be performed using 29,4 kN (3 000 kgf) load, a 10 mm indenter, and the standard dwell time of 10 s to 15 s.

8.5 In some cases, maximum allowable hardness values are provided in both HRC (or HRBS) and HBW. In those instances, either scale may be used.

8.6 When hardness requirements are stated in HBW, and testing using stationary Brinell hardness equipment is not viable, testing shall be performed using the comparison hardness test method (commonly, but incorrectly, referred to as portable Brinell hardness testing).

8.7 When applicable, the conversion tables in ASTM E140 or ISO 18265 shall be used for conversion of hardness values obtained by other test methods to HRC, HRBS, or HBW values. However, tables for many materials do not exist in those standards. The tables should be used only for materials that are specifically listed. Conversions may be performed based on empirical data for materials that are not covered when approved by the end user. When converted hardness values are used, they shall be reported in accordance with the requirements specified in ASTM E140 or ISO 18265.

8.8 Sufficient hardness tests shall be made to establish the actual hardness of the material being examined. Individual hardness readings exceeding the specified value shall be considered acceptable if the average of several readings taken within close proximity does not exceed the specified value and no individual reading exceeds the specified value by more than 2 HRC (or by more than 5 % in the case of HBW or HV 10).

8.9 Acceptance criteria for microhardness testing using Knoop or Vickers hardness test methods (see ASTM E384) are outside the scope of this International Standard. See Annex B for more information.

8.10 The use of portable hardness testing methods to verify compliance with the requirements of this International Standard is prohibited unless explicitly approved by the end user. The one exception that does not require end user approval is the use of comparison hardness testing in accordance with ASTM A833 to evaluate weld deposits as specified in NACE SP0472 (see Annex B).

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9 Procedure for the addition of new materials or processes

9.1 General balloting requirements

New materials and/or processes may be balloted based on field experience and/or laboratory test data.

9.2 Field experience data requirements

9.2.1 Field experience data shall document the alloy composition(s), condition(s), and hardness level(s), the process fluid parameters that influence SSC, and the exposure history.

9.2.2 In certain alloy families (such as duplex stainless steels), microstructure is also a critical variable, and shall also be documented.

9.3 Laboratory test data requirements

9.3.1 The laboratory testing of materials shall be performed in accordance with NACE Standard TM0177. If actual service conditions are outside these limits, SSC of approved materials may be possible.

9.3.2 The candidate material shall be tested in accordance with the test procedures established in NACE Standard TM0177. The tensile bar, C-ring, bent beam, and double-cantilever beam test specimens described in NACE Standard TM0177 are accepted test specimens. Any of these test specimens may be used.

9.3.3 A minimum of three test specimens from each of three different commercially prepared heats shall be tested in the condition balloted for inclusion. The composition of each heat and the heat treatment(s) used shall be furnished as part of the ballot. The candidate material's composition range and/or UNS number and its heat-treated condition requested for inclusion in this International Standard shall be included with the ballot.

9.3.4 The hardness of each test specimen shall be determined and reported as part of the ballot. The average hardness of each test specimen shall be the hardness of that test specimen. The minimum test specimen hardness obtained for a given heat/condition shall be the hardness of the heat/condition for the purpose of balloting. The maximum hardness requested for inclusion of the candidate material in this International Standard shall be specified in the ballot and shall be supported by the data provided.

9.3.5 In certain alloy families (such as duplex stainless steels), microstructure is also a critical variable, and shall also be documented for each heat/condition.

9.3.6 For each of the tests performed, the testing details shall be reported as part of the ballot item being submitted.

10 New restrictions and deleted materials

10.1 The revision process may be used to impose new restrictions on materials or to delete materials from this International Standard. New restrictions may include such items as imposition of a maximum hardness requirement, reduction of a maximum hardness requirement, elimination of a previously acceptable heat-treatment condition, and elimination of a previously acceptable manufacturing process.

10.2 Affected materials in use at the time of the change that complied with a prior edition of this International Standard and that have not experienced sulfide stress cracking (SSC) in their current application are considered in compliance with this International Standard.

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10.3 When affected metallic materials as discussed in 10.2 are eventually removed from their current application, replacement materials shall be compliant with the current edition of this International Standard, except that new equipment manufactured from affected materials, as well as equipment refurbished using new components manufactured from affected materials, may be qualified for use in specific applications in accordance with Clause 11.

11 Qualification of unlisted alloys, conditions, and/or processes for specific applications

11.1 Alloys, conditions, and processes that are not listed in this International Standard may be qualified for use in specific sour applications. Clause 11 provides the minimum requirements for compliance with this International Standard when unlisted alloys, conditions, and/or processes for specific applications are qualified.

11.2 The end user shall be responsible for determining the suitability of an unlisted alloy, condition, and/or process for a specific application based on laboratory test data, field experience, and/or risk-based analysis.

11.3 If laboratory testing is used as an acceptance basis, testing should be performed in accordance with accepted standard test methods such as those documented in NACE Standard TM0177.

11.4 If field experience and/or risk-based analysis is used as an acceptance basis, a number of factors should be considered.

a) The stress level, material form, forming process, heat-treatment condition, microstructure, and mechanical properties (particularly hardness) of the field experience specimen should be well documented.

b) The environmental conditions to which the field experience specimen is exposed should be well documented.

c) The field experience exposure time should be adequate to ensure that the unlisted alloy, condition, and/or process provide resistance to SSC.

11.5 The suitability of the unlisted alloy, condition, and/or process for a specific application should be determined based on an evaluation of the environmental conditions in the intended specific application compared with the environmental conditions in the laboratory tests and/or the field experience.

11.6 The composition, material form, forming processes, heat-treatment condition, and mechanical properties of equipment manufactured using an unlisted alloy, condition, and/or process should be controlled based on the corresponding information for the laboratory test specimens and/or field experience specimens.

11.7 Unlisted alloys, conditions, and/or processes qualified for specific applications based on the requirements in Clause 11 shall not become part of this International Standard unless they are approved through the ISO balloting process.

12 Standard road map

For ease of use, Table 1 provides general information by material/application group, as well as references to specific clauses that cover applicable material and fabrication requirements.

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