By Don Bush

Welding
of Carbon Steel Materials for Use in Sour Service

Valve manufacturers often are required to provide valves for use in wet H_2S, or “sour” environments. While NACE MR0175 is commonly specified for valve constructions destined for sour oil or gas production applications, there are several other industry standards that document appropriate materials and processing practices for sour services. In the case of carbon steels, these documents provide much more detailed information than MR0175.

Valve manufacturers are commonly required to provide valves for use in environments containing hydrogen sulfide (H_2S) and water, environments that are often referred to as "sour". NACE MR0175, Material Requirement - Sulfide Stress Cracking Resistant Metallic Materials for Oilfield Equipment, is usually specified for valve constructions destined for sour oil or gas production applications. However, there are several other industry standards and reports that document appropriate materials and processing practices for materials for sour services. In the case of carbon steels, these documents provide much more detailed information than MR0175. This article provides a brief background on sulfide stress cracking, summarizes metallurgical considerations related to carbon steel weldments, and provides an overview of some of the key points in NACE RP0472 and NACE Committee Report 8F192.

Sulfide Stress Cracking and Wet H_2S Cracking Mechanism

In essence, steels above a certain hardness are susceptible to a phenomenon known as hydrogen embrittlement. Hydrogen embrittlement is defined as "a condition of low ductility in metals resulting from the absorption of hydrogen."[1] Hydrogen embrittlement is mainly a problem in steels with ultimate tensile strength greater than 90 ksi, and is usually manifested by delayed, catastrophic, brittle fracture at tensile stresses well below the ultimate tensile strength of the material.

When steel corrodes in an environment containing water and H_2S, the H_2S breaks down to form H^+ ions and S^- ions. Since H^+ ions are much smaller than H_2 molecules, they can easily diffuse into steels at ambient temperatures. The S^- ions react with the steel surface to form a porous iron sulfide layer. This iron sulfide layer catalyzes the absorption of H^+ ions into the steel, resulting in a higher degree of hydrogen charging than would occur in an environment with H^+ ions and no catalyst. Cracking in the presence of H_2S corrosion is usually called "sulfide stress cracking" in the oil and gas production industry, and "wet H_2S cracking" in the oil refining industry. The term "wet H_2S cracking" is more descriptive of the actual mechanism and will be used throughout the remainder of this article.

In order for wet H_2S cracking to occur, three conditions must be met:

1. The hardness/strength of the material must be above a threshold value;
2. The hydrogen concentration in the steel must achieve a threshold value; and
3. The material must be subjected to a tensile stress above a threshold value.

In all cases, all of these factors are interrelated. In other words, as the value of one factor increases, the threshold value of the other factors decreases. There are no well-established rules regarding these interrelationships. However, guidelines have been developed with respect to H_2S content in the process fluid. If the H_2S content and certain other factors are met (such as the presence of liquid water), the application is deemed to be "sour". Guidelines have also been developed for materials and material conditions that are acceptable for sour applications. The most widely known guideline document is NACE MR0175. NACE MR0175 restricts carbon steels to a maximum hardness of 22 Rockwell "C" (HRC), and to the following heat treat conditions:

(a) hot-rolled
(b) annealed
(c) normalized
(d) normalized and tempered
(e) normalized, austenitized, quenched, and tempered
(f) austenitized, quenched, and tempered.

The standard mechanical property requirements for the typical carbon steel pressure vessel materials, such as ASME SA216 WCB, WCC, LCB, and LCC castings, SA105 and SA350 LF2 forgings, SA515 Grade 70 and SA516 Grade 70 plate, etc., essentially ensure that the bulk properties will meet MR0175 requirements.

Why Weldments Are a Concern

Carbon steels are all hardenable by heat treatment to some degree. Carbon steels are hardened by a two-step heat treating process known as austenitizing and quenching. The austenitizing phase involves heating the steel to above a critical temperature, which changes it from its ambient-temperature equilibrium structure (ferrite and pearlite in the case of carbon steels) to an austenitic structure. Quenching involves cooling the steel at a rate that is rapid enough to prevent the formation of the ferrite and pearlite equilibrium microstructure. The structure that is formed is a metastable atomic arrangement called martensite. Martensite is very hard and strong, but is generally somewhat brittle.

A further operation, called tempering, is often performed after austenitizing and quenching. Tempering involves heating the steel to a temperature below the critical temperature, which causes the formation of a softer, tougher microstructure that is weaker than the untempered martensite, but stronger than the equilibrium ferrite and pearlite structure.

The maximum hardness that can be achieved by a particular steel, referred to here as the hardness potential, is strongly dependent upon the carbon content. Alloying elements, such as chromium, nickel, molybdenum, manganese, etc., generally serve to increase the hardness potential, but to a much lesser degree than the carbon content.

On the other hand, the ease with which the hardness potential is realized upon quenching, known as hardenability, is heavily influenced by alloying elements other than carbon. For example, a steel with 0.22% carbon has a hardness potential of well over 50 HRC. However, only very thin sections of strip or small wire can be quenched in water rapidly enough to form 100% martensite and achieve the hardness potential in a plain carbon steel. The addition of small amounts of manganese, chromium, nickel, molybdenum, and other elements increases hardenability tremendously. The effects of alloying elements are so dramatic that steels with only two percent alloying elements can form fully martensitic structures when air-cooled from the austenitizing temperature.

The reason that heat treatment of steels is pertinent to welding is that the deposited weld filler metal, and the heat-affected zone (HAZ) in the base metal, undergo this same type of "heat treatment" during the welding process. As a weld deposit is produced, the deposit starts as a molten puddle. The puddle quickly solidifies as heat is transferred to the surrounding base metal. Immediately after solidification, the weld deposit is well above the critical temperature. In addition, the base metal immediately adjacent is also heated to above the critical temperature. As the weldment cools by heat transfer into the surrounding base metal and atmosphere, the weldment is being "quenched". The actual cooling rate is dependent upon a number of factors, including:

- The size of the weld deposit (smaller size = faster cooling);
- The mass of the base metal (larger/heavier = faster cooling); and
- The temperature of the base metal (cooler = faster cooling).

Because of this built-in quenching process, weldments can potentially contain localized hard regions in the weld deposit, the HAZ, or both.

Chemistry Controls vs. Weldment Hardness

The as-welded hardness achieved in the weld deposit and the HAZ is dependent upon three factors:

1. The hardness potential of the material (weld filler and base metal);
2. The hardenability of the material (weld filler and base metal); and
3. The cooling rate.

If the right (or wrong) combination of hardness potential, hardenability, and cooling rate exist, high hardness can occur in as-welded deposits and/or in the HAZ.

Restricting the maximum carbon content to a lower value than that normally allowed for the material (example: 0.22% maximum carbon vs. the normal 0.25% maximum carbon for WCC) reduces the hardness potential for the material. In other words, the maximum hardness the weldment could possibly achieve in the as-welded condition is lower.

The carbon equivalent (CE) is defined by the following equation:

$$\mathrm{CE} = \%\mathrm{C} + \frac{\%\mathrm{Mn}}{6} + \frac{(\%\mathrm{Ni} + \%\mathrm{Cu})}{15} + \frac{(\%\mathrm{Cr} + \%\mathrm{Mo} + \%\mathrm{V})}{5}$$

The carbon equivalent attempts to account for both hardness potential and hardenability in one parameter that can be used to assess weldability of steels. Thus, controlling the CE to a lower value reduces the likelihood of hard regions in the as-welded condition under a given set of welding conditions.

The cooling rate is affected by part configuration and welding parameters. Carbon content restriction and CE limits do not affect cooling rate.

Industry Standards for Wet H_2S Cracking Prevention in Carbon Steels

The potential for hard zones in weldments has been recognized in both the oil and gas production industry and the oil refining industry. The production industry's document, NACE MR0175, contains the following paragraph pertaining to this issue:

> "5.3.1.2 Welding procedure qualifications on carbon steels that 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 ensure that the procedure is capable of producing a hardness of 22 HRC maximum in the condition in which it is used."

Some manufacturers and users interpret this paragraph to mean that any procedure qualification that includes hardness readings in the weld deposit, HAZ, and base metal meets the intent of the paragraph above. However, the important words in the above paragraph are not those regarding the hardness traverse, but rather the words "use controls other than stress relieving". Whereas the specific controls that may be required are left up to the manufacturer, some type of extra control measures are implied.

The ASME construction codes (ASME Boiler and Pressure Vessel Code, ASME B31.1 Power Piping, ASME B31.3 Process Piping, and ASME B31.5 Refrigeration Piping) provide rules that govern PWHT of carbon steel weldments based upon the section thickness being welded. Thinner sections may be welded without PWHT, whereas thicker sections *(actual limits vary by specific code)* require PWHT. Unfortunately, the ASME codes don't require any correlation between the carbon content or CE level of the PQR specimen and that of the production base metal. In other words, it is perfectly acceptable within the ASME codes to utilize a PQR specimen with 0.12% carbon and a CE of 0.35 to qualify a non-PWHT procedure for welding any P-1 material. This is in spite of the fact that some P-1 materials have maximum carbon contents of 0.35% and can produce CE values exceeding 0.60. Thus, it is logical that the "controls other than stress relieving" mentioned in MR0175 would likely need to include some type of correlation between the carbon content or CE level of the PQR specimen and that of the production base metal.

In addition, the term "hardness traverse" is not defined in MR0175. In general, a hardness traverse consists of a series of hardness indentations regularly spaced along a line. In weldments, hardness traverses are generally run along lines that are parallel to the surface of the base metal. Lines are generally located just below the surface *(common values are 1 mm or 0.060" below the base metal surface)*, through root passes, and/or through the weldment at the centerline of the base metal thickness. Hardness measurements at random locations in the three zones do not constitute a hardness traverse, but rather represent a "hardness survey". Finally, most user specifications that actually define the hardness traverse require that reading be taken using 10kg Vickers or Rockwell 15N scale so the readings will be more sensitive to local hard spots than if Rockwell "C" or Brinell scales were utilized.

The refinery industry's document, "NACE RP0472, Recommended Practice - Methods and Controls to Prevent In-Service Environmental Cracking of Carbon Steel Weldments in Corrosive Petroleum Refining Environments," contains various alternative methods that can be followed to assure that carbon steel weldments will be soft enough to resist cracking.[2] To summarize briefly, the document deals with two separate issues—weld deposit hardness and base metal heat-affected zone hardness.

Weld deposit hardness is addressed as follows: —The accepted method is to perform portable Brinell tests on weld deposits to ensure that they meet a 200 HB maximum requirement. The weld deposit hardness testing requirement is waived when the SMAW welding process is used with E60XX or E70XX fillers or when the GTAW welding process is used with ER70S-X fillers (other than -6, -7, or -G grades).

Although RP0472 does not specifically address postweld heat treatment (PWHT) as a means for controlling weld deposit hardness, it is generally recognized as an effective method. The PWHT method involves tempering at a temperature high enough to reduce hardness and relieve residual welding stresses via high-temperature stress relaxation. Thus, PWHT has a positive effect on two of the three factors influencing wet H_2S cracking. PWHT is effective at reducing the hardness of nearly any carbon steel weld deposit to well below the hardness levels recommended to prevent wet H_2S cracking.[3] However, RP0472 cautions that the practice of postweld heat treating at lower temperatures for longer times, as allowed by some of the ASME Codes, should not be followed when the heat treatment is being performed to reduce the hardness of the weld deposit or the heat-affected zone.

There are three methods listed in RP0472 for control of base metal heat-affected zone hardness:

- Chemistry control (specifically, control of the maximum carbon equivalent);
- Weld procedure qualification hardness testing, including less-restrictive chemistry control in conjunction with special welding process controls; and
- Postweld heat treatment (PWHT), also commonly called stress relieving.

The chemistry control method involves selection of filler metal chemistry in conjunction with control of the base metal carbon equivalent to such a low level that low weld deposit hardness and HAZ hardness is virtually guaranteed regardless of welding process parameters. NACE Committee Report 8X1944 states that a CE of 0.43 is commonly specified for base materials when this technique is employed.

The weld procedure qualification hardness testing method is a variant of the chemistry control method. In this method, a less restrictive maximum CE value may be chosen for production base metal. A welding procedure qualification record (PQR) test specimen is then created using actual production material or a coupon of representative material with an actual CE corresponding to the maximum CE value that is to be applied to the production base material. Welding variables (such as preheat, current, voltage, travel speed, interpass temperature, etc.) are controlled and monitored closely during the creation of the procedure qualification specimen. The PQR tests include a hardness traverse using either 10kg Vickers or Rockwell 15N scale. Predefined hardness traverse diagrams are provided for several weld geometries ***(See Figure 1)***.

The resulting welding procedure specification (WPS) then must contain certain restrictions to ensure that the PQR specimen is actually representative of production weldments. Those restrictions include:

- The procedure may only be used with the same base metal grade and class. In other words, a procedure qualified on A516 Grade 60 plate material could not be used to weld A516 Grade 70 plate material or A216 Grade WCC castings, even though all are within the same ASME Section IX P-Number group.
- The actual CE of production material must be controlled to a value less than or equal to that of the PQR specimen.
- The heat input used during production welding must not

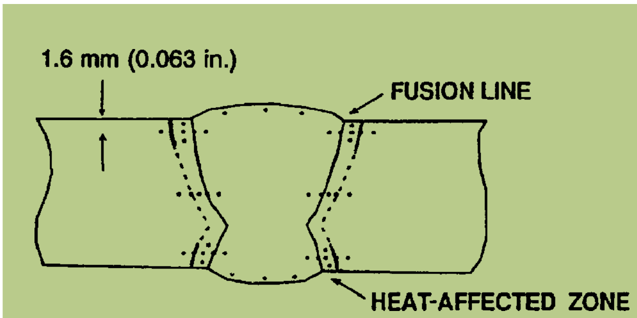
deviate from the heat input used during creation of the PQR specimen by more than 10% lower or 25% higher (alternatively, for the shielded metal arc welding (SMAW) process, the maximum bead size and the minimum length of weld bead per unit length of electrode used in creation of the PQR specimen can be imposed as a requirement in the WPS).

- Preheat and interpass temperatures must be at least as high as those utilized in production of the PQR specimen.
- If preheat was not utilized for the PQR specimen, the maximum base metal thickness of production weldments must not be allowed to exceed the thickness of the PQR specimen.
- Other restrictions apply to fillet welds, submerged-arc welding (SAW), gas metal arc welding (GMAW), flux-cored arc welding (FCAW) processes, welding procedures involving bead-tempering techniques and other techniques that are sensitive to weld-bead sequence, and materials containing intentional additions of microalloying elements such as Nb (Cb), V, Ti, and B.

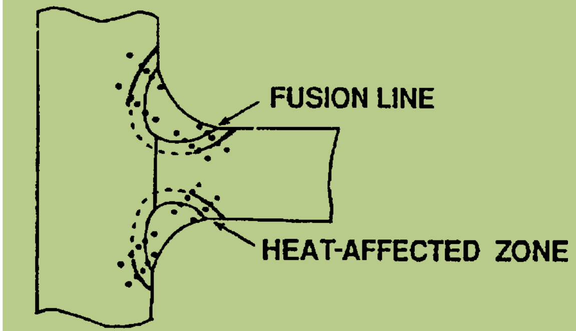
The postweld heat treatment (PWHT) method involves tempering at a temperature high enough to reduce hardness and relieve residual welding stresses via high-temperature stress relaxation. Thus, PWHT has a positive effect on two of the three factors influencing wet H_2S cracking. Furthermore, except in cases where carbon steel base metals are intentionally micro-alloyed with certain strengthening elements, PWHT is effective at reducing the hardness of any welded carbon steel pressure vessel material to well below the hardness levels recommended to prevent wet H_2S cracking. Again, RP0472 cautions that the practice of postweld heat treating at lower temperatures for longer times, as allowed by some of the ASME Codes, should not be followed when the heat treatment is being performed to reduce the hardness of the weld deposit or the heat-affected zone.

Discussion and Comparison of Methods

Products procured for new oil and gas facilities, expansions, and/or repairs often are governed by customer or contractor piping specifications. These specifications may contain stipulations requiring maximum CE values for all components in the piping system, and these requirements are often imposed on valves. The use of these special chemistry controls allows the company and/or its contractors to perform welding on components without PWHT and be reasonably sure that weld heat affected zones will be soft enough to resist wet H_2S cracking. This is especially useful for components that will be actually welded into the system, although it is also beneficial for non-welding-end components that may eventually require welding to repair erosion or corrosion damage.



Butt Weld



Fillet Weld

Figure 1: Schematics from NACE RP0472 showing suggested locations for hardness traverse indentations. Copyright 1995 by NACE International. All rights reserved by NACE: reprinted by permission. NACE standards are revised periodically. Users are cautioned to obtain the latest edition; information in an outdated version of the standard may not be accurate.

The special chemistry control approach works very well for pipe and for vessels fabricated from plate materials, where it is often difficult to perform postweld heat treatment. Economically, it is often not that expensive to use special materials for these applications because entire mill runs of material will be specifically produced to satisfy the order for raw material.

On the other hand, most valves are made from castings. In most cases, a special order for controlled CE does not comprise an entire heat of material. This increases the cost and lead time of the castings significantly, since a special heat must be prepared. In addition, it is difficult to procure custom forgings and other wrought products often used in valve fabrications with special CE limits because most vendors supplying these materials to valve companies don't make their own raw materials. Rather, must search for raw materials that meet the special requirements.

In addition, most valves are designed to be used in a multitude of applications in a wide variety of industries—oil and gas, electric power, chemical, pulp and paper, etc. Weldment hardness is not as critical an issue in general applications as it is in wet H_2S applications. Therefore, it isn't

	Hardness Control Method		
	Low CE Controls on Base Metal (eg.: 0.43 max CE)	**Weld Procedure Qualification Hardness Testing + Intermediate CE Control on Base Metal + Welding Process Controls**	**Postweld Heat Treatment**
Material cost	Highest cost	Higher cost	Standard cost
Lead time	Longest lead time	Longer lead time	Standard lead time
Welding controls	Standard welding controls	Very restrictive welding controls. Heat input control requirements may be very difficult to maintain with manual welding processes.	Standard welding controls
PWHT	Not required	Not required	Required
Resulting weld deposit hardness	Acceptable, provided proper filler metals are utilized	Acceptable, provided proper filler metals are utilized	Lower than other methods
Weld deposit hardness tests	Required except for some SMAW and GTAW welds	Required except for some SMAW and GTAW welds	Not necessary
Resulting HAZ hardness	Acceptable, intermediate hardnesses	Acceptable, likely higher hardnesses than other methods	Acceptable, lowest hardnesses of all methods
Residual stress level	Higher	Higher	Lower
Weld repairs to correct erosion or corrosion damage	Require no PWHT or special welding process controls	Require postweld heat treatment(a)	Require postweld heat treatment
Weld deposit hardness tests on weld repairs	Should be performed except for some SMAW and GTAW welds(b)	Not necessary (assuming PWHT is performed)	Not necessary
Residual stress level adjacent to repairs	Higher	Lower	Lower

(a) *Assumes weld repairs performed by refinery or contract welders will not be performed with special welding procedures developed for intermediate carbon and/or CE controlled chemistry*

(b) *Since PWHT will not be performed, hardness testing would be prudent when utilizing fillers which would normally be tested. However, hardness testing of erosion or corrosion repair welds is often difficult or impossible because they are usually located internally.*

economically attractive to standardize on a special, more expensive casting chemistry to accommodate the small percentage of valves that are destined for sour service.

With respect to valves that are not weld-end products *(such as flanged, wafer, and screwed-end valves)*, special compositional restrictions are only beneficial if the valves ever require welding. During manufacture of the valve, welding may be performed either for fabrication purposes or to repair casting or machining defects. In most cases, it is probably less expensive to postweld heat treat welded valves destined for sour service than to purchase special chemistries that would allow welding without PWHT. After the valves have been in service, welding may be utilized to repair erosion or corrosion damage. Again, in many cases, it may actually be more economical to postweld heat treat repairs or, in the case of smaller valves, simply replace the valves, than to purchase special chemistry controls in the original valves.

Finally, postweld heat treatment provides the additional benefit of reducing residual stresses in the weld deposit, the heat-affected zone, and the adjacent base metal. Therefore, in addition to providing lower hardnesses than the other methods, it also reduces overall stresses in the weldment, which further enhances its wet H_2S cracking resistance. Whereas CE controls minimize the probability that weld heat-affected zones will contain hard spots, residual welding stresses are not reduced whatsoever by CE controls.

There is a widespread belief that postweld heat treatment is often not practical on finished carbon steel valve bodies. Whereas this may be true in specific cases, postweld heat treatment is actually performed on a routine basis on finished carbon steel bodies with excellent success. Prior heat history of the body castings usually results in a low enough stress state that distortion beyond design drawing tolerances does not occur.

The table to the left briefly summarizes the major advantages and disadvantages of the three approaches.

Summary

Carbon steel valves are commonly used in oil and gas production and refinery applications where they must be resistant to cracking in environments containing water and H_2S. There are several industry standards and documents available that contain requirements and/or recommendations for welding of carbon steels destined for sour service, including NACE MR0175, NACE RP0472, and NACE Committee Report 8X194.

The requirements listed in NACE MR0175 for carbon steels welded without subsequent PWHT are not very specific. NACE RP0472, in conjunction with Committee Report 8X194, documents several methods that can be used to ensure carbon steel weldments will be soft enough to resist cracking in wet H2S environments. Those methods include hardness testing of weld deposits, postweld heat treatment, control of base metal CE to levels low enough to ensure low HAZ hardness, and weld procedure qualification hardness testing in conjunction with control of CE to intermediate levels and detailed welding process controls to ensure low HAZ hardness.

Conclusions

Each of the hardness control methods has advantages and disadvantages. The selection of the most robust and economically attractive method depends upon several factors, including the available equipment, available welding procedure specifications, product forms (castings, plate, pipe, forgings, etc), and availability of heat treating equipment.

In the case of valves, postweld heat treatment is an attractive method for preventing hard spots in weldments. It provides the secondary benefit of reducing residual stresses which can contribute to wet H_2S cracking. Low CE requirements are an effective method for preventing hard spots in welds. However, low CE requirements increase raw material costs and lead time significantly, and have no beneficial effect on residual stresses generated by welding. Weld procedure qualification hardness testing, utilized in conjunction with intermediate CE requirements and restrictive welding process controls, does not appear to be a generally effective solution. Based upon the cost and lead time factors and the very restrictive welding process control requirements, this approach would probably be optimum only in very specific situations.

If not for the cost and lead time issues surrounding the low CE control method, this approach would obviously be very popular and effective. A possible solution to this dilemma would be the development of ASTM standard carbon steel materials with a low carbon equivalent value (such as 0.43 maximum) as a requirement. For example, if a grade "WCD" were added to ASTM A216 (and ASME SA216) with this maximum CE requirement, and if valve companies were to adopt this new material their "standard" valve body material, it would eventually be no more expensive than a standard carbon steel body today.

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Footnotes

[1] NACE Standard MR0175-2000, "Sulfide Stress Cracking Resistant Metallic Materials for Oilfield Equipment", NACE International, Houston, TX, 2000.

[2] NACE Standard RP0472-1995, "Methods and Controls to Prevent In-Service Environmental Cracking of Carbon Steel Weldments in Corrosive Petroleum Refining Environments", NACE International, Houston, TX, 1995.

[3] Shargay, C., "Overview of NACE International Standard RP0472", Paper No. 417, NACE Corrosion/99, NACE International, Houston TX, 1999.

[4] NACE Technical Committee Report 8X194, "Materials and Fabrication Practices for New Pressure Vessels Used in Wet H2S Refinery Service", NACE International, Houston, TX, 1994.