

Hydrocarbon Contamination and Diffusible Hydrogen Levels in Shielded Metal Arc Weld Deposits

Oil contamination of basic H4 and H4R SMAW electrodes removes low-hydrogen characteristics on contact, and conventional baking treatments for humidity and water exposure restore electrodes to approximately the H8 designation

BY B. M. PATCHETT AND M. A. R. YARMUCH

ABSTRACT

Published literature suggest the avoidance of hydrocarbon contamination (oil or grease) of shielded metal arc welding (SMAW) electrodes to prevent diffusible hydrogen cracking in weld zones, but there are no published data on the contamination mechanisms of exposure to hydrocarbons on the diffusible hydrogen level. This paper explores hydrocarbon contamination of low-hydrogen basic SMAW electrodes. Contact with oil causes instant and gradually increasing contamination and diffusible hydrogen levels with time, and the contamination is greater with lower oil viscosity. Standard reconditioning heat treatment for water contamination lowers the diffusible hydrogen content to about H8 levels for the electrodes and oils investigated.

Introduction

The presence of hydrogen in ferritic steels welded by the shielded metal arc welding (SMAW), submerged arc welding (SAW), flux cored arc welding (FCAW), and other flux-bearing processes has been studied for many years. The studies have concentrated on humidity and moisture effects on absorbed hydrogen levels. Hydrogen-assisted cracking (HAC) in hardenable steel weld zones is controlled by several methods — electrode flux chemistry and conditioning, procedure control (a combination of suitable preheat and heat input) in steels of relatively low hardenability, and the addition of postweld heat treatment (PWHT) on steels of high hardenability (carbon equivalent) (Ref. 1). The strength level and microstructure of low-carbon steels has emerged as another criterion (in addition to hardness) governing the susceptibility to HAC (Ref. 2). In both cases, the amount of diffusible hydrogen imparted to the weld zone is of importance in determining suitable procedural parameters. Initial assessment of the amount of diffusible hydrogen imparted

to weld deposits by various welding processes was hampered by imprecision in the measurement of the diffusible hydrogen in the deposited weld metal. This was traced to the varying solubility of molecular hydrogen in the liquid media used to collect the hydrogen expelled by a weld sample (Ref. 3). Standardized tests based on the use of a liquid without measurable solubility (mercury) or vacuum extraction produced accurate and reproducible results (Refs. 4, 5). In these extraction tests, results are conventionally reported as “mL/100 g deposited weld metal,” which is a characteristic of the hydrogen collection method, not of atomic hydrogen levels in the actual weld deposit. This paper uses a dual reporting system including parts per million (ppm), a more relevant number for atomic hydrogen in solid solution. There is only approximately a 10% differ-

ence, for example 10 mL/100 g equating to 11 ppm. This difference is often within the typical variability of results in electrode testing.

The International Institute of Welding (IIW) designation system for hydrogen potential of welding consumables are “very low” for up to 5 mL/100 g; “low” for 5–10 mL/100 g; “medium” for 10–15 mL/100 g; and “high” for more than 15 mL/100 g of weld metal deposited. The American Welding Society assesses electrodes via a logarithmic scale for diffusible hydrogen levels in a weld deposit. H16 is for 16 mL/100 g of weld metal (17.6 ppm), H8 is for an electrode producing less than 8 mL/100 g (8.8 ppm), the common upper limit for “low hydrogen,” and H4 is for less than 4 mL/100 g or 4.4 ppm. Commercial consumables that are able to reduce the diffusible content further down the logarithmic scale (2 or 1 mL/100 g) are not reliable at present for arc welding processes involving fluxes (SMAW, FCAW, and SAW). AWS A5.1, *Specification for Carbon Steel Electrodes for Shielded Metal Arc Welding*, was revised in 2004 to reflect this new optional (voluntary) designation system. The specification also permits an optional supplemental “R” suffix designator for electrode coverings that satisfy absorbed moisture limitations. Note that the H16, H8, and H4 designations should not be confused with the H1 (extra-low hydrogen ≤ 5.5 ppm or 5 mL/100 g), H2 (low-hydrogen ≤ 11 ppm or 10 mL/100 g), and H3 (hydrogen not controlled) designations in AWS D1.1 Annex XI for assessment of hydrogen cracking susceptibility via the Pcm method.

Attempts to connect weld metal diffusible hydrogen to moisture in the flux (Ref. 6) and weight gains during exposure to humidity met with higher variability in the results. This is due to the fact that weight gain is partially due to carbon dioxide absorption (Ref. 7). Water exists in most low-hydrogen fluxes in the following

KEYWORDS

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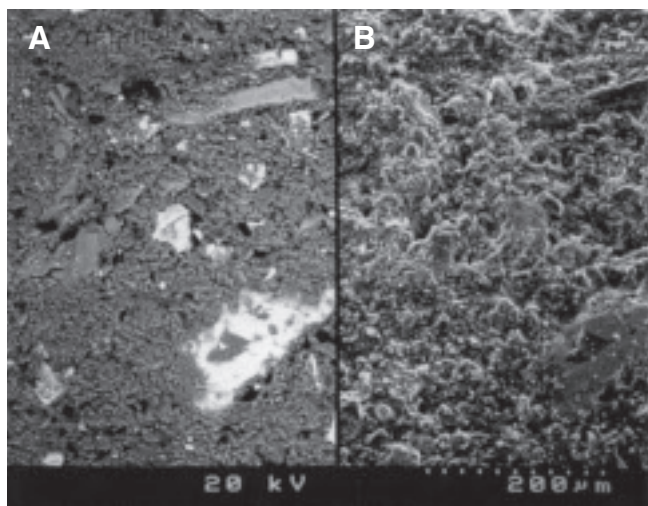


Fig. 1 — Flux structure of standard basic low-hydrogen electrodes. A — Cross section; B — surface.

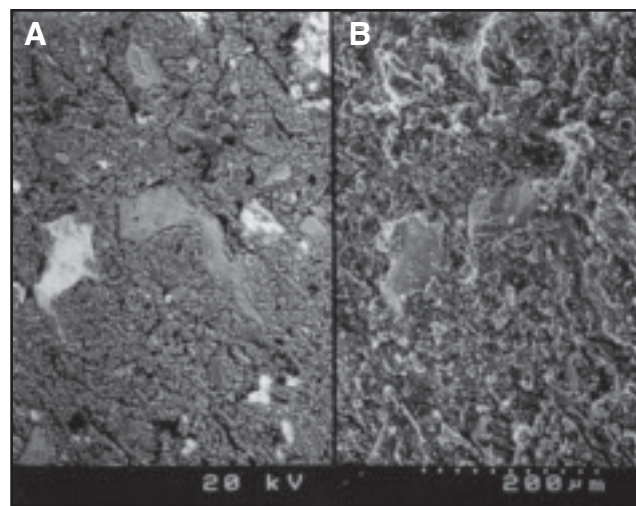


Fig. 2 — Flux structure of low moisture pickup basic low-hydrogen electrodes. A — Cross section; B — surface.

two forms: water of crystallization in binders or agglomeration stabilizers and adsorbed water via hygroscopic components in the flux. The former is “permanent,” in the sense that total removal destabilizes the mechanical integrity of the flux, while the latter is transitory and can be removed without destabilizing the flux. This dual behavior limits the temperature of baking to approximately 400°–425°C. Published information on the subject of water content concerns the relationship between water uptake and exposure conditions, including steps to follow to minimize or reduce the net amount of deposit diffusible hydrogen. Since the water from exposure appears to be adsorbed (surface) rather than absorbed (bulk) by the flux, part of the water is dispersed into the atmosphere by resistance heating of the SMAW electrode during welding, and adsorbed water adds less diffusible hydrogen than does bound water (Ref. 8). The substantial efforts of several investigators, over many years, has shown that the diffusible hydrogen content of SMAW deposits is related strongly to water content of the flux up to approximately 0.3% water, but the relationship becomes more scattered at higher water contents (Refs. 9, 10). Diffusible hydrogen is also affected by atmospheric humidity at the point of welding, which is more noticeable in low-hydrogen electrode deposition than it is in electrodes producing higher hydrogen levels (Ref. 9). An equation (Ref. 9) is available that relates diffusible hydrogen to atmospheric humidity and flux water content, which is considered accurate up to about 0.3% adsorbed and crystalline water:

$$H_D = [260a_1 + 30a_2 + 0.9b - 10]\%$$

where H_D = IIW diffusible hydrogen in mL/100 g; a_1 = as-baked coating moisture %; a_2 = adsorbed moisture %; and b = atmospheric humidity in mm Hg.

This equation strictly applies only to the electrodes tested (manufactured in Japan) and must be used with circumspection if differing flux chemistries from other manufacturing sites are used.

These numerous investigations into the effects of humidity, adsorbed water, and water of crystallization are not matched by investigations into the effects of hydrocarbon contamination, although the deleterious effects of oil and grease contamination on diffusible hydrogen content are generally assumed. This paper is intended to provide an initial assessment of the effects of hydrocarbon contamination on diffusible hydrogen only. Complex hydrocarbons may contain other elements of interest, such as sulfur, but further investigation is necessary to study other possible contaminants.

Experimental Program

The electrodes used in the experimental program were of the E4918 (E7018)

type, 4 mm ($\frac{1}{8}$ in.) in diameter. Both standard and moisture-resistant (low moisture pickup (LMP)) types were assessed. All electrodes were conditioned at 375°C (707°F) for 1 h before use. Cooled and weighed electrodes were then immersed in a graduated cylinder to 25 mm (1 in.) from the top of the flux coating in two single viscosity grade mineral lubricating oils of differing viscosity, a 10-W low-viscosity grade and a 30-W medium-viscosity grade. Multigrade oils were avoided to isolate any effect of viscosity. After various times of immersion, excess oil was stripped from the flux covering with a 1.5-mm- ($\frac{1}{16}$ -in.-) thick flexible rubber grommet squeegee containing a hole slightly smaller in diameter than the electrode coating. The slight pressure ensured a consistent removal of surface oil. Immediate weighing determined the weight gain caused by oil immersion. Since the “dry” electrode weight varied, weight gain was defined as a percentage gain for each electrode, rather than an absolute weight gain. Welding behavior/diffusible hydrogen measurements followed within 5 min. Procedural conditions were 24 V, 190 A on electrode positive polarity and a welding speed of 200

Table 1 — Chemical Composition of Electrode Fluxes

Element	Percentage Standard Electrode	Percentage Low Moisture Pickup Electrode	Percentage Change—Standard to Low Moisture Pickup
Silicon	17.8	14.4	-23
Potassium	15.5	10.9	-42
Calcium	57.0	54.0	-6
Titanium	0.0	12.7	+ X
Manganese	3.5	3.8	+9
Iron	5.9	3.7	-55
Total	>99	>99	

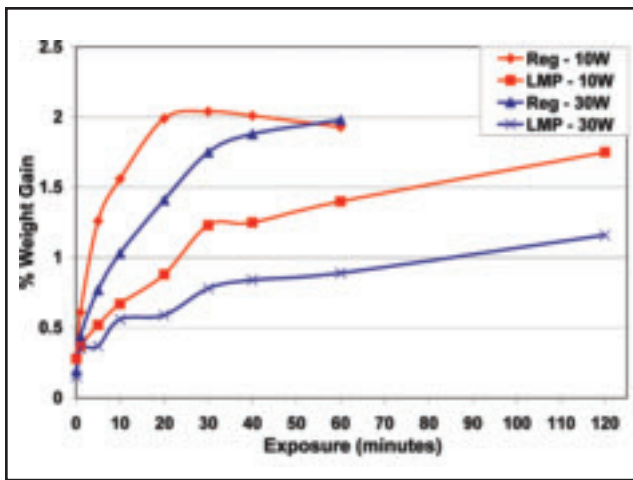


Fig. 3 — Weight gain vs. exposure time during electrode immersion.

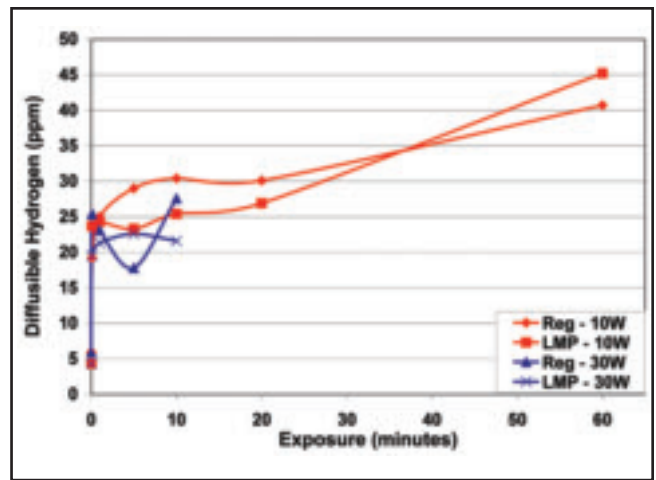


Fig. 4 — Weld deposit diffusible hydrogen content vs. hydrocarbon exposure time.

mm/min, producing a heat input of 1.4 kJ/mm. Bead-on-plate (BOP) welds were produced on ASTM A36 steel pads 10 mm ($\frac{3}{8}$ in.) thick, 75 mm (3 in.) wide, and 300 mm (12 in.) long with the SMAW process to assess electrode usability characteristics after oil contamination. Weld metal diffusible hydrogen levels were determined on IIW specimens under mercury according to ISO 3690. Bakeout after hydrocarbon contamination was identical to the conditioning procedure, 375°C for 1 h.

Results and Discussion

The diffusible hydrogen contents were determined for each electrode type after conditioning to establish a base line for comparison with oil contamination levels. The standard electrodes produced an average diffusible hydrogen level (3 determinations) of 5.9 ± 1.1 ppm or 5.4 mL/100 g and the LMP types an average of 4.3 \pm 0.7 ppm or 3.9 mL/100 g.

Before assessing the oil adsorption characteristics, the surfaces of the electrode fluxes were inspected in a scanning electron microscope (SEM) to assess the particle size and structure of the flux coatings. The standard electrode flux dis-

played discrete mineral particles of diameters ranging from about 50 to 300 micrometers in a fine matrix. The LMP flux was similar but had smaller average particle size and many small cracks in the matrix. A fractured surface of each flux showed that each contained porosity between the various mineral particles. The surface features and internal structures of the two fluxes are shown — Figs. 1, 2. The results show that the flux coatings are small-scale analogs of porous rock formations.

The chemistry of each flux type was assessed in the SEM at the same time using energy-dispersive X-ray (EDX) analysis (Table 1).

The chemistry of the fluxes is not a complete and detailed analysis (e.g., no determination of oxygen was made), but there are significant differences, particularly the titanium level. This suggests that the rutile level is increased in the LMP flux. The mineral constituents are therefore somewhat different, as might be expected. This strongly suggests that behavior during hydrocarbon exposure may vary from one manufacturer's flux to another, or from country to country, as demonstrated previously in assessing the effects

of moisture (Ref. 9).

The results show that the adsorption of oil by the flux coating causes a very rapid initial weight gain by the electrode coating. An increase in viscosity produces a lower weight gain for a given time of immersion — Fig. 3. Long immersion times of up to 24 h slightly increase weight gain. This is probably an indication of saturation or a stable balance between oil penetration and entrapped air in the surface and subsurface pores in the extruded flux coating.

Studies of crude oil movements through porous rock have shown that permeation depends inversely on viscosity (Ref. 13) and that surface-active components dominate adsorption, with the higher molecular weight fractions adsorbing preferentially (Ref. 14). Mineral oils used for lubrication are usually paraffinic oils, which have long chain molecular structures. Higher-viscosity oils have longer molecular chains on average. In the interaction between porous rock and oil alone, the adsorption behavior is polar and the more surface-active elements of the oil are adsorbed (Ref. 12). The molecules are typically in the C_{20} to C_{70} range (number of carbon atoms in a molecule), and the boiling point is in excess of 370°C. Molecules in the C_{15} to C_{50} range (diesel fuel) boil at temperatures between 300° and 600°C (Ref. 15), indicating that the higher average molecular weight molecules in lubricating oils would have an even wider range of boiling temperature. Therefore, the normal bakeout temperature range for basic low-hydrogen electrodes (350°–400°C) may cause boiling of the lower molecular weight fractions, but not all of the higher molecular weight fractions.

There is an instant increase in dif-

Table 2 — Bakeout Effects on Diffusible Hydrogen Levels

Electrode	Oil Type	Exposure Time	Diffusible Hydrogen from Contact		Diffusible Hydrogen after Baking	
			mL/100 g	ppm	mL/100 g	ppm
Standard	10 W	0.1 min	17.3	19.2	5.2	5.8
Low Moisture Pickup	10 W	0.1 min	21.3	23.7	4.8	5.3
Low Moisture Pickup	10 W	24 h	40.7	45.2	5.7	6.3
Low Moisture Pickup	30 W	24 h	—	—	6.9	7.7

fusible hydrogen levels after contact between the oil bath and flux coatings. Short-term immersion results show that the diffusible hydrogen level jumps to about 20 ppm or 18 mL/100 g after only a few seconds of contact with the oil — Fig. 4. Long-term immersion increased the weight gain incrementally, and an apparent saturation level was reached. The diffusible hydrogen results reflect this, with the maximum of about 40–50 ppm (36–45 mL/100 g) appearing for oil exposure time up to 24 h. This is similar to diffusible hydrogen results for Exx10-type cellulosic electrodes.

Baking reduces the diffusible hydrogen in the weld deposits substantially, as shown in Table 2, to the IIW “low-hydrogen” (5.5–11 ppm) diffusible hydrogen level but cannot restore full IIW “very-low hydrogen” behavior. On the AWS logarithmic scale, the results are at or below, the H8 designation. The diffusible hydrogen content after baking for the specific electrodes assessed is similar for both electrode coating types, both oil viscosities, and is also similar for any contamination time from 0.1 min to 24 h.

The postbaking SMAW process behavior during manual operation was acceptable for the welder and did not produce any visual flaws in BOP welds, e.g., pinholes or cracks, which were the expected results from the H8 levels of diffusible hydrogen. No formal weldability tests were conducted due to the potentially large size of a comprehensive alloy assessment program.

Conclusions

1. Contact between basic low-hydrogen SMAW electrodes and oil causes instant and incrementally increasing contamination by adsorption, leading to significantly increased diffusible hydrogen levels in deposited weld metals.

2. Diffusible hydrogen levels from contaminated electrodes are above about 18 mL/100 g or 20 ppm for any time of contact and for both electrodes and both oil viscosities used in this investigation.

3. Weight gain from contact with hydrocarbons is reduced by higher oil viscosity, which shows that larger molecules penetrate less rapidly. Oil thus appears to be adsorbed by the electrode flux.

4. The low-moisture-pickup flux, intended to resist adsorption of water, also reduced the rate at which oil is adsorbed, possibly by minimizing flux porosity and flow passage access.

5. Baking electrodes contaminated by oil at a typical temperature and time recommended for adsorbed water removal reduces the net diffusible hydrogen levels to the 5–10 ppm range, corresponding to IIW “low-hydrogen” rather than IIW

“very low-hydrogen” behavior. In terms of the logarithmic AWS scale, baking causes a reduction in diffusible hydrogen to approximately the H8 level.

6. The inability of baking to completely reverse oil adsorption is likely due to a combination of molecular fraction boiling temperatures and bonding of higher molecular weight fractions to pore surfaces in the flux during adsorption.

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