Behavior of Hydrogen in Arc Weld Pools

Very little, if any, hydrogen is rejected by the weld pool solidification process

BY D. G. HOWDEN

ABSTRACT. A study was made of the transport of hydrogen, dissolved in a stationary arc-melted pool, into and through the adjacent solid metal. For all materials investigated, the concentration of hydrogen in the surrounding metal was greatly in excess of equilibrium values as measured by the internal solution pressure, which attained values much higher than the partial pressure of hydrogen in the arc.

It is postulated that this supersaturation is caused by a "pumping" action of the molten pool involving a mechanism of repeated solidification and remelting of the metal in the outer layers of the pool caused by instability of the arc. Based on this model, it was postulated that very little hydrogen is rejected during the solidification process. When welding, with a moving pool and high solidification rates, it is suggested that even less gas would be rejected and that this mechanism plays a much less significant role in the formation of weld metal hydrogen porosity than is popularly believed.

Introduction

The fact that hydrogen plays an important role in the underbead cracking at low alloy steel weldments and the formation of certain types of weld metal porosity is well established. The gas, originating from electrode coverings or contamination of the welding materials with water vapor or organic material, dissolves in the liquid metal weld pool from the arc atmosphere and contributes to porosity in the molten pool or diffuses into the heat-affected zone (HAZ) of steel to enhance cracking.

The mechanism by which hydrogen enters the HAZ and contributes to cracking is not fully understood. However, in recent years progress has been made towards the understanding of gas/metal reactions under the complex conditions existing in the arc. This was accomplished by investigating the absorption processes which occur in the relatively simple gas tungsten arc system and stationary "weld pools." By making controlled hydrogen additions to the arc atmosphere, investigators were able to study both the rate of absorption of gas and the steady state hydrogen content of arc-melted pools (Ref. 1, 2).

A model was proposed (Ref. 2) for a mechanism consistent with the experimental observations. Briefly, hydrogen is rapidly absorbed into the high temperature "active" zone where the arc impinges on the pool and a rapid equilibrium of gas/metal solubility is achieved. Electromagnetic stirring action in the pool then transports the hydrogen-saturated liquid metal to cooler regions of the pool. Since the solubility of gas decreases with temperature, the solution becomes supersaturated to produce high internal solution pressures which are responsible for porosity formation in the pool and represent the driving force for the diffusion of hydrogen to the HAZ.

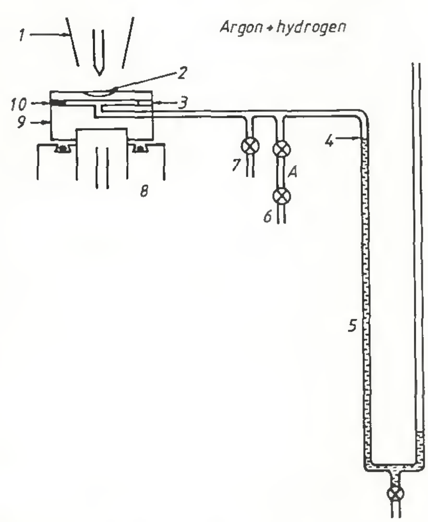

Fig. 1—Diagram of experimental apparatus: 1—GTA torch shielding gas; 2—molten weld pool; 3—silver braze; 4—zero volume; 5—mercury manometer; 6—air or gas; 7—vacuum; 8—water-cooled anode assembly; 9—copper block; 10—specimen; A—calibrating volume

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The present investigation was carried out to study the transport of hydrogen, dissolved in a stationary arc-melted pool, from the pool into the surrounding solid metal. Of particular interest was the behavior of hydrogen during the solidification process and the concentration of gas to be expected in the HAZ's of welds.

Experimental Technique and Procedure

The experimental technique consisted of melting a pool on the upper surface, and at the center, of a disc of metal 25 mm (1 in.) diameter and 3 mm (0.12 in.) thick and measuring the permeation of hydrogen through the disc. The equipment is shown schematically in Fig. 1. The pool was melted using a gas tungsten arc welding torch, and the disc was supported on a water-cooled copper block designed to keep the underside of the disc solid and avoid "fall through" of the pool. The disc was silver brazed to the copper block around the circumference to produce a gastight joint.

The pressure of gas on the underside of the disc was measured on a mercury manometer connected to the volume between the disc and the copper block via a small hole in the block. This space could be evacuated and was of known volume.

The procedure consisted of starting

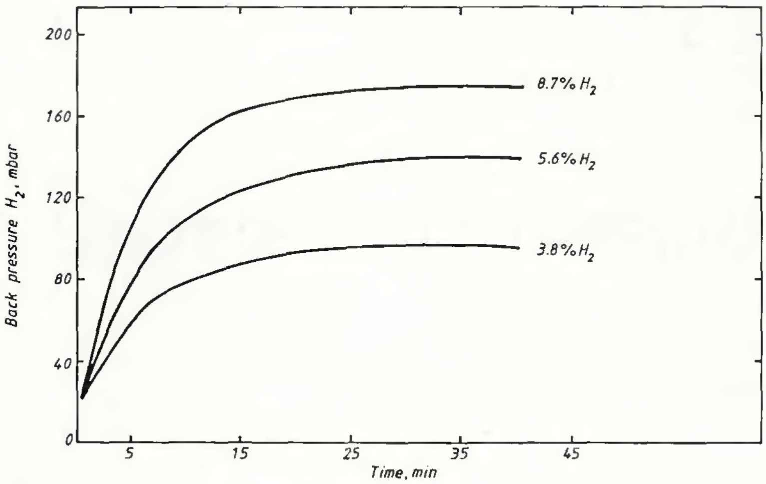

Fig. 2 — Typical hydrogen back pressure buildup curves

the gas tungsten arc in pure argon and evacuating the reverse side volume, finally closing off the pumps when there was no pressure rise. The selected argon-hydrogen gas mixture was then passed through the arc and the buildup of hydrogen "back pressure" measured on the manometer as a function of time until a steady state pressure was obtained — Fig. 2. In several instances a check of the equipment was made by allowing the hydrogen to permeate the disc in the opposite direction (leaving a vacuum) when the hydrogen was removed from the arc shielding gas.

Specimens of mild steel and Type 18-8 stainless steel were examined for limited conditions. A more detailed study was made of the hydrogen behavior in commercially pure nickel which proved to be more suitable for long duration arc times. Shielding gas compositions of up to 10% hydrogen in argon and arc currents of 50-350 A were used for an arc length of 3 mm (0.12 in.).

Experimental Results

The results are divided into two parts dealing with the effect of shielding gas hydrogen content and arc current respectively on the steady state back pressure of hydrogen.

Effect of Shielding Gas Composition

The effect of hydrogen partial pressure in the arc on the back pressure is shown in Figs. 3 — 5 for specimens of mild and stainless steel and nickel. In all instances,

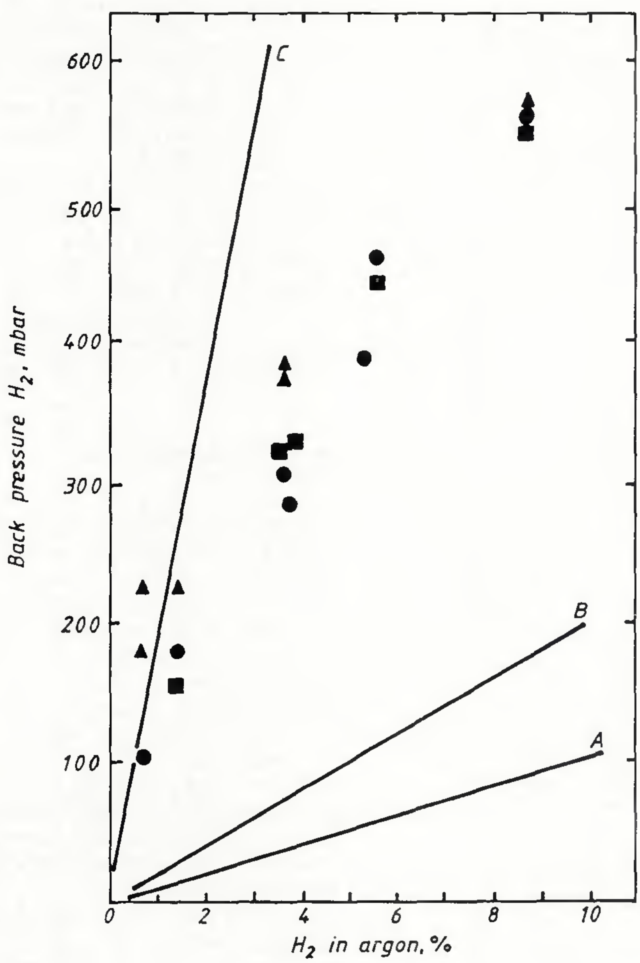

Fig. 3 — Effect of hydrogen partial pressure in arc on back pressure for mild steel: A — hydrogen partial pressure in arc; B — hydrogen pressure corresponding to 1.4 supersaturation (Ref. 2); C — theoretical pressure produced by quenching 1.4 supersaturated liquid to delta ferrite at melting point. Current in amperes: triangles — 100; circles — 180; squares — 250

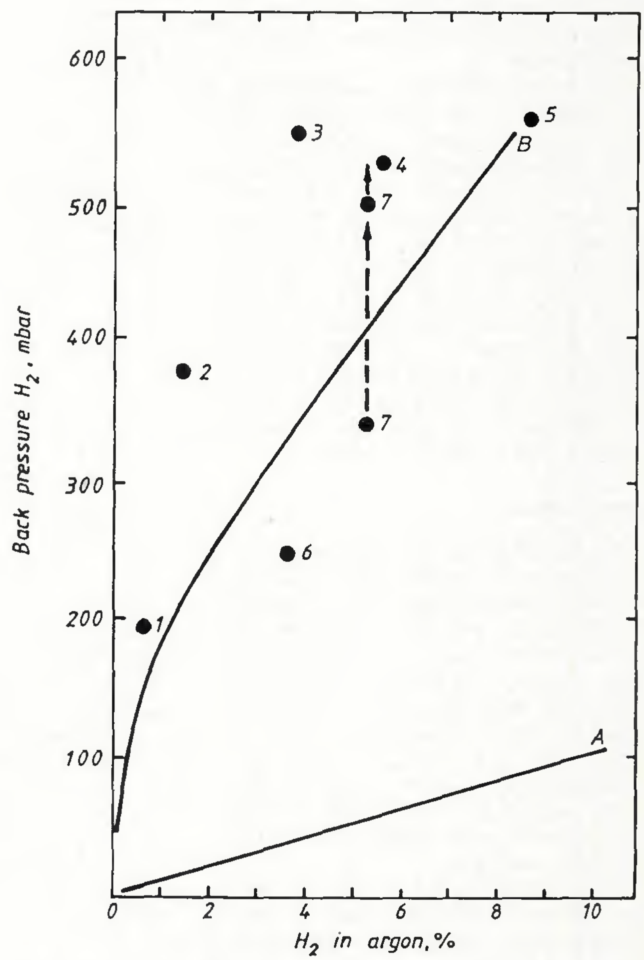

Fig. 4 — Effect of hydrogen partial pressure in arc on back pressure for Type 304 18-8 stainless steel, 180 amperes: A — hydrogen partial pressure in arc; B — mean curve for mild steel (Fig. 3). Numbers refer to order of experimental determination; determination no. 7 described further in Fig. 6

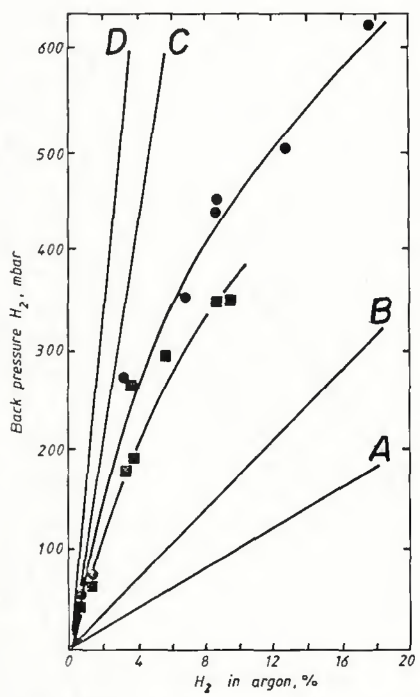

Fig. 5 — Effect of hydrogen partial pressure in arc on hydrogen back pressure for nickel: A — hydrogen partial pressure in arc; B — hydrogen pressure corresponding to 1.3 supersaturation (Ref. 2); C — theoretical pressure produced by quenching supersaturated liquid to solid at melting point; D — theoretical pressure produced by quenching 1.3 supersaturated liquid to solid at melting point. Current in amperes: circles — 200; squares — 300

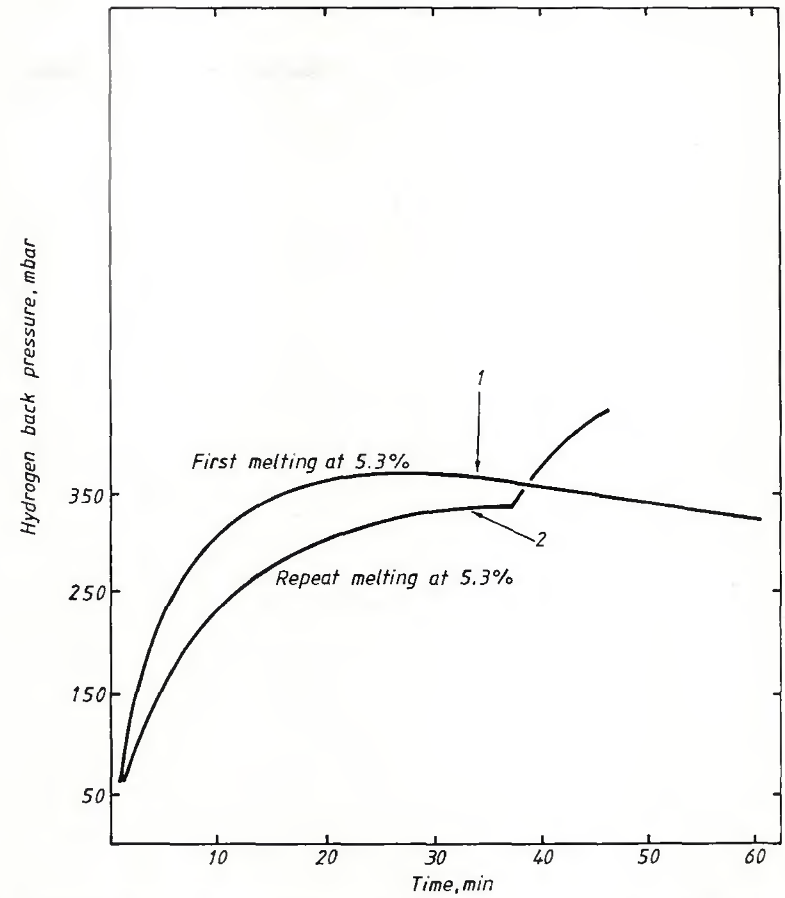

Fig. 6 — Effect of holding time and addition of new material to pool on hydrogen back pressure for stainless steel: 1 — no new material added; 2 — new material added. 200 amperes; argon with 5.3% hydrogen

the pressure of hydrogen achieved on the underside of the specimen increased with hydrogen content of the shielding gas, but greatly exceeded the actual pressure of hydrogen in the arc (by about a factor of 5 to 7 over the range of hydrogen pressures investigated).

The behavior of stainless steel was quite different from that of mild steel and nickel, however. The magnitude of the back pressure depended on the number of determinations carried out on the specimen, as indicated by the number sequence shown in Fig. 4. Of particular interest is determination number 7, where it was noted that the steady state back pressure decreased with time of melting and could be restored in magnitude by the addition to the pool of small amounts of new material — Fig. 6. The stainless steel also gave off considerable vapor which condensed around the molten pool. Chemical analysis gave the composition of the vapor as 13%Cr-3%Ni-25% Mn.

Effect of Arc Current

For an arc atmosphere containing 8.7% hydrogen in argon, the steady state back pressure was investigated as a function of arc current in the range 50 to 350 A for a nickel specimen. The results are shown in Fig. 7 where it may be observed that the pressure decreases with arc current to a minimum around 300 A. It was noticed that the rate of attaining steady state pressure was very low at low currents.

Diameters of the upper pool surface were measured as a function of current and converted to areas in Fig. 8. Under the conditions of melting employed, the molten pool was initiated at 50 A and grew in area proportionally with current. In addition, it was observed that the arc gyrated on the pool at a frequency of about one revolution per three seconds(s), causing the solidified pool area to appear greater than that of the actual molten pool area at any instant.

Discussion of Results

In all instances the pressure of hydrogen measured on the reverse side of the disc was appreciably greater than that in the arc. It is apparent, therefore, that the arc or pool acts as a pump forcing hydrogen from the liquid pool into the surrounding solid metal. To explain this, the earlier work on hydrogen absorption must be considered (Ref. 1, 2).

According to Sievert's Law the amount of hydrogen dissolved in a metal, at a given temperature, is given by:

$$V = S\sqrt{P} \qquad (1)$$

where V is the hydrogen, concentration, mlitre/100 g; S is the solubility for a pressure of hydrogen of 1 atmosphere, mlitre/100 g; P is the pressure of hydrogen in atmospheres.

Consequently, the internal solution pressure

$$P = \left[\frac{V}{S}\right]^2 \qquad (2)$$

Considering a stationary arc-melted pool of metal, it has been shown that hydrogen in the arc atmosphere dissolves in the high temperature molten metal under the arc according to the relationship

$$V_A = S_A\sqrt{P_o} \qquad (3)$$

where V_A is the hydrogen concentration; S_A is the high temperature solubility; P_o is the partial pressure of hydrogen in the arc.

It was also shown that, as a result of the stirring action of the current in the molten pool, the concentration of hydrogen in the whole pool attains the level of that in the high temperature zone. At the outer perimeters of the pool, however, where the temperature is much lower

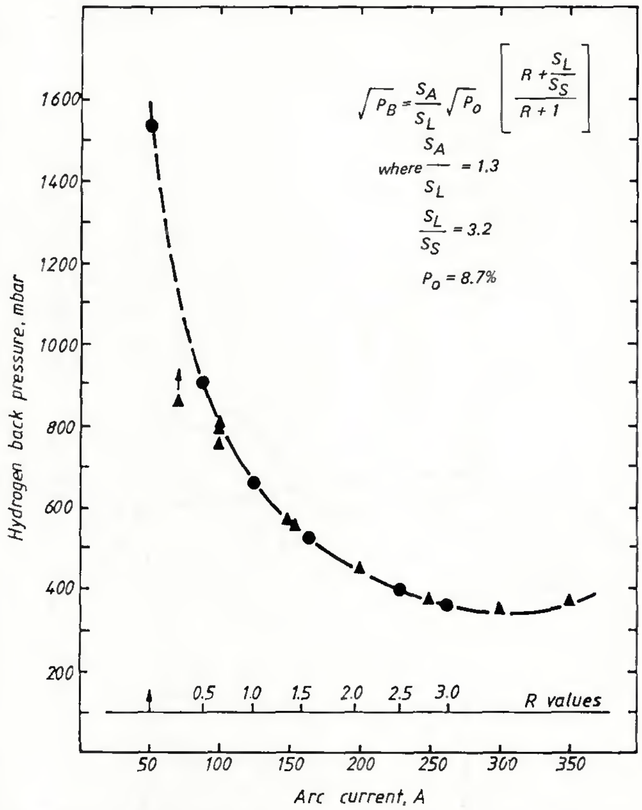

Fig. 7 — Effect of arc current on hydrogen back pressure of nickel (experimental) and fitting points from eq. (9) (theoretical) using arbitrary R values. Triangles — experimental points; circles — theoretical values, P_B

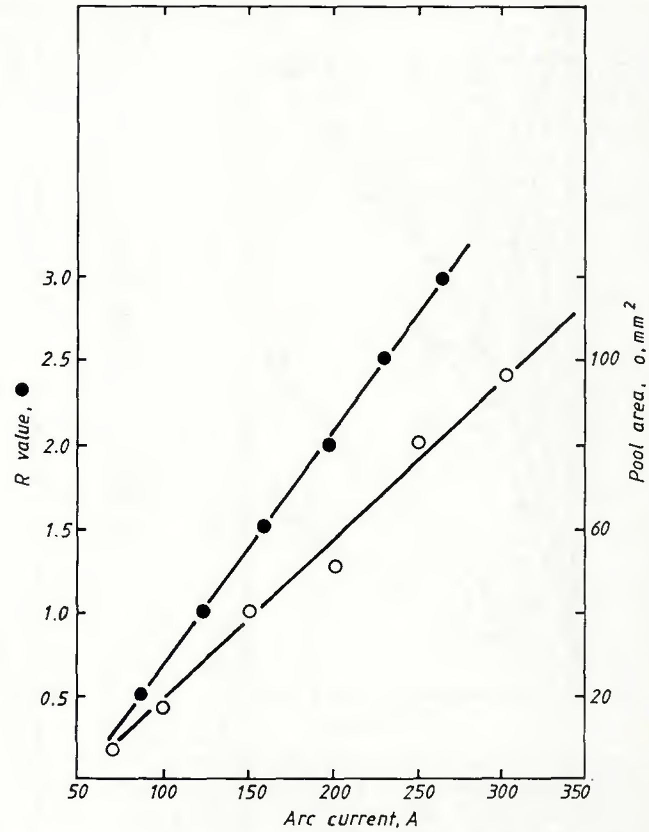

Fig. 8 — Combined plot of pool upper surface area (experimental) and R values from Fig. 7 as a function of arc current for nickel specimen and shielding gas composition of argon with 8.7% hydrogen

(approching the melting point of the material) the solubility, S_L, of hydrogen is lower, and thus the hydrogen internal solution pressure, P_L, is greater:

$$P_L = \left[\frac{V_A}{S_L}\right]^2 = \left[\frac{S_A}{S_L}\right]^2 P_o \qquad (4)$$

For the materials investigated, S_A/S_L cannot exceed approximately 1.5 (Ref. 2). Hence the above reasoning will not fully explain the measured pressures of 5 to 7 times greater than the pressure of hydrogen in the arc.

Greater pressures could be created, however, if the liquid metal with hydrogen concentration (V_L or V_A) were to be solidified, thereby reducing the hydrogen solubility to S_S at a temperature just below the melting point. The internal solution pressure of hydrogen in the solid metal, P_S, would then be:

$$P_S = \left[\frac{V_L}{S_S}\right]^2 = \left[\frac{S_A}{S_S}\right]^2 P_o \qquad (5)$$

Since the ratio S_A/S_S is approximately equal to 6 for iron and 4 for nickel, P_S values would be of the order of 36 or 16 times greater than P_o respectively for iron and nickel. The measured back pressures, P_B, therefore lie between the S_A/S_L and S_A/S_S values, suggesting that some hydrogen must be trapped in a supersaturated solid solution during solidification.

It is suspected that the gyration of the arc observed on the stationary weld pool was responsible for cyclical melting and solidifying the outer layers of the pool, producing a pumping effect as illustrated in Fig. 9.* This action would provide the explanation of why the concentration of hydrogen and its related solution pressure would be abnormally high. The experimentally measured values were lower than those for the theoretical maximum and it is postulated that the explanation lies in the chosen specimen configuration and a difference in permeation rates of hydrogen.

According to eq. (5), if S_A and S_S remain relatively constant as the current and pool size change, the measured back pressure, P_S, should be proportional to the hydrogen partial pressure in the arc, P_o. From Figs. 3–5 this does not appear to be the situation. It is believed that increasing both the hydrogen content of the shielding gas and arc current leads to changes of molten pool shape which

**Many transformer-rectifier power supplies also produce (Ref. 3) a ripple of sufficient magnitude to cause a cyclic solidification/melting phenomenon.*

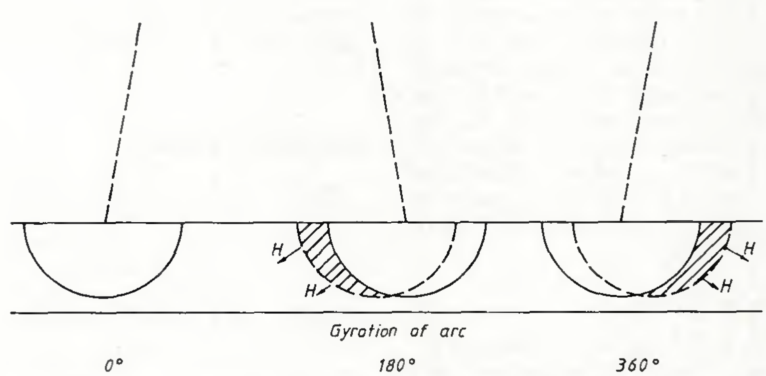

Fig. 9 — Schematic representation of proposed mechanism for "pumping" hydrogen by "stationary" arc-melted pool. Shaded areas are newly solidified and supersaturated with hydrogen

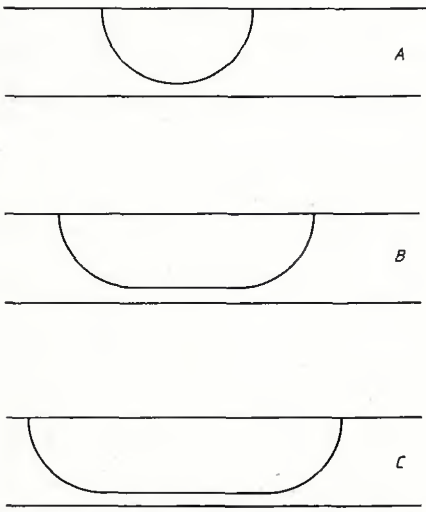

Fig. 10—Diagram depicting probable change of pool shape with increasing arc heat input

reduce the theoretical back pressure, P_S, to the lower, measured back pressure, P_B, in the following way:

As heat input increases as a result of the hydrogen content of the arc atmosphere or arc current, the pool would be expected to expand in a two-dimensional manner (restricted by the water-cooled copper backup) once a near full penetration pool had been achieved—Fig. 10. The back pressure would then be determined by a balance of the forward rate of hydrogen entry through the pool and the backward rate of hydrogen escaping through the pool and adjacent hot metal.

Rates of permeation of hydrogen through a membrane may be expressed by:

$$\text{Rate} = \frac{GA}{D}\sqrt{P} \tag{6}$$

where G is the permeation constant; A is the area of permeation; D is the thickness of the membrane; P is the molecular driving pressure. Referring to Fig. 11 and making some approximations:

$$\text{Forward rate} = \frac{G_1 A_1}{D_1} \cdot \frac{S_A}{S_L}\sqrt{P_o} + \frac{G_2 A_2}{D_2} \cdot \frac{S_A}{S_S}\sqrt{P_o} \tag{7}$$

$$\text{Backward rate} = \frac{G_1 A_1}{D_1}\sqrt{P_B} + \frac{G_2 A_2}{D_2}\sqrt{P_B} \tag{8}$$

Inserting rate constants X and Y for particular steady state conditions of the pool and equating the forward and backward rates where:

$$X = \frac{G_1 A_1}{D_1} \quad \text{and} \quad Y = \frac{G_2 A_2}{D_2}$$

$$\sqrt{P_o} \cdot \left[X \cdot \frac{S_A}{S_1} + Y \, \frac{S_A}{S_S}\right] = \sqrt{P_B} \cdot \left[X + Y\right]$$

$$\text{or } \sqrt{P_o} \cdot \left[R + \frac{S_L}{S_S}\right] = \frac{S_L}{S_A}\sqrt{P_B} \cdot \left[R + 1\right]$$

$$\text{where } R = \frac{X}{Y} = \frac{G_1 A_1 D_2}{G_2 A_2 D_1}$$

$$\text{whence } \sqrt{P_B} = \frac{S_A}{S_L} \cdot \sqrt{P_p} \cdot \left[\frac{R + \frac{S_L}{S_S}}{R + 1}\right] \tag{9}$$

Assignment of values to G, A, and D is very difficult for the system studied, although reasonable values may be inserted for S_A, S_L, and S_S for the hydrogen in nickel system. A correlation between eq. (9) and the experimental variation of back pressure with current is possible, however. Values of back pressure have been calculated for arbitrary values of R for appropriate values of P_o,

Table 1—Nomenclature Used in Equations (4) to (9)

V_A	—	hydrogen concentration in the high temperature region of the pool under the arc
V_L	—	hydrogen concentration in the liquid metal at the melting point
S_A	—	solubility of hydrogen in the high temperature region of the pool under the arc
S_L	—	solubility of hydrogen in the liquid metal at the melting point
S_S	—	solubility of hydrogen in the solid metal at the melting point
P_o	—	partial pressure of hydrogen in the arc atmosphere
P_B	—	pressure of hydrogen measured on the back side of the specimen
P_S	—	solution pressure of hydrogen in the solid metal at the melting point
G	—	hydrogen permeation constant
R	—	the ratio of the geometrical permeation rate constants operative at the central and peripheral regions of the pool

$$R = \frac{G_1 A_1 D_2}{G_2 A_2 D_1}$$

[see Fig. 11 and eqs. (7) to (9)]

S_A, S_L and S_S, and the curve was fitted to the experimental curve shown in Fig. 7. The curves fit well over the range of current from 100 to 300 A, and the relationship between R values and arc current is linear over this range with R approaching zero at 50 A where the pool area also approaches zero—Fig. 8.

However, as the pool becomes very small, then:

$$(A_1 \rightarrow 0)\ R \rightarrow 0 \text{ and } P_B = \left[\frac{S_A}{S_S}\right]^2 \cdot P_o.$$

This would imply that, during solidification, the concentration of hydrogen in the solid nickel remains the same as that in the liquid producing full theoretical internal solution pressure ($P_B = P_S$) and that no rejection of hydrogen occurs on solidification. Experimental values never reached this level because the rate of pressure buildup was slow. Extrapolating the curve to R = 0, however, predicts full theoretical back pressure ($P_B = P_S$) estimated to be 1520 mbar for nickel.

As the pool increases in size, the back pressure would be expected to decrease until R approaches infinity (A_1 is much larger than A_2) whence

$$P_B = \left[\frac{S_A}{S_L}\right]^2 \cdot P_o \text{ or } 148$$

mbar for P_o = 88 mbar

Figure 7 shows that the back pressure achieved a minimum value of about 333 mbar as R increased. This effect is attributed to the constraints of the experimen-

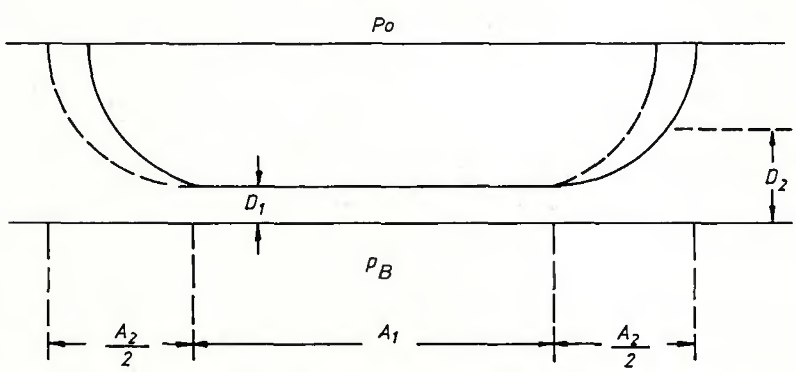

Fig. 11—Diagram showing nomenclature required in equations (7) and (8). P_o—partial pressure of hydrogen in arc; P_B—reverse side hydrogen pressure

tal specimen, which did not allow the pool to expand indefinitely because of the strong cooling effect around its circumference.

The results obtained from this investigation provide useful information applicable to the understanding of the behavior of hydrogen in weldments. Traditionally it has been understood that a sizable portion of the hydrogen in the molten pool was rejected by the solid metal during the solidification process. The present investigation suggests that this is not so.

Figure 12 represents the instantaneous solution pressure change when a system (nickel in this instance), originally under steady state conditions of hydrogen solution and consisting of liquid and solid metal, is changed by the solidification of a thin layer of the liquid. The solution pressure of hydrogen in the solidified layer is increased by a factor of $(S_L/S_S)^2$ and hydrogen will diffuse both into the solid metal adjacent to the pool and back into the molten pool. Since it is likely that the rate of solidification for a practical, moving weld pool would be greater than that because of arc oscillations in a stationary pool considered in this work, it seems very likely that rejection of hydrogen into the molten pool would not take place and that the initial concentration of hydrogen in the solidified weld metal would be the same as that in the molten weld pool. This being so, the traditional explanation of porosity formation by rejection of hydrogen by the solidification front would need to be re-evaluated.

The unusual behavior of stainless steel is interesting. Apparently the major vapor loss from the pool was of manganese representing at least 50% of the original pool content. A significant difference in the ability of the pool to "pump" hydrogen was noted.

More data need to be obtained, but two explanations are possible. The more probable explanation relates to the change of concentration of an element such as manganese, affecting one or both of the ratios S_A/S_L or S_L/S_S in eq. (9). This suggests that small changes of alloying element concentrations may change the amount of hydrogen absorbed by weld metals.

The other explanation would relate a change of pool shape and, hence, diffusion geometries, to a relative change of absorption and desorption rates. The latter seems less likely since only very small additions of the new material were very effective in raising the back pressure. Also, referring to Fig. 7, when no metal addition was made, the rate of pressure drop took place much faster than one could imagine evaporation changing the geometry of the pool.

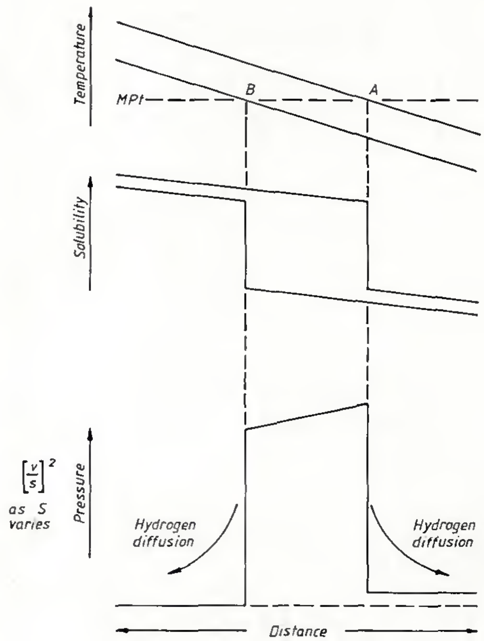

Fig. 12 — Diagram showing how increased hydrogen solution pressure can be attained by movement of solid/liquid interface causing hydrogen to diffuse both into liquid and solid zones adjacent

Conclusions

From the investigation of the behavior of hydrogen in stationary arc-melted pools of mild steel, stainless steel, and commercial purity nickel it was concluded that:

1. Very little, or no, hydrogen is rejected by the solidification process and that, for practical welding conditions with a moving weld pool, the initial hydrogen content of the solidified weld metal is probably equal to that of the molten pool for arc atmospheres consisting of up to 10% hydrogen in argon

2. The amount of hydrogen absorbed by the weld metal can be greatly affected by relatively small changes in weld metal composition

3. Popular theories of hydrogen porosity formation which rely on the increase of hydrogen concentration in the molten metal arising from rejection of hydrogen by the solidification front should be re-evaluated

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