WELDING RESEARCH

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An Evaluation of Rapid Methods for Diffusible Weld Hydrogen

Hydrogen extraction time is reduced drastically by elevating temperature up to 400°C

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ABSTRACT. An evaluation has been carried out of rapid methods for measuring diffusible weld hydrogen, and the results have been compared with those of the primary room temperature mercury method. Different analytical techniques have been studied looking at extraction temperatures of up to 400°C (752°F), while a range of consumable types for shielded metal arc (SMA), flux cored arc (FCA) and submerged arc welding (SAW) deposits was included. With the exception of welds containing porosity, satisfactory agreement with the primary method was obtained at temperatures up to 400°C, provided appropriate care was taken. Analysis times were markedly reduced from 14 to 21 days at 20°C (68°F) to ~ 30 min at 400°C.

Introduction

The risk of hydrogen cracking in ferritic steel welds depends on a number of interrelated factors, but the amount of hydrogen introduced during welding is of prime importance. In designing a welding procedure to avoid cracking, it is necessary to define the hydrogen level associated with a given welding consumable, using a standard test method (Ref. 1). Hydrogen exists in two forms in a weld deposit at room temperature, namely, diffusible and residual. It is the diffusible hydrogen fraction that is traditionally measured when characterizing the hydrogen content in a weld deposit by a given welding consumable, and the most widely accepted primary test method for measuring it uses collection over mercury at ambient or near ambient temperatures (Ref. 2).

In some standards, *e.g.*, BS 6693: Part 1: 1986 (Ref. 3), the collection of the diffused hydrogen for three days over mercury is required. However, it has been shown that figures based upon three days collection time are low by a variable and unpredictable amount, which may be as much as 20% of the diffusible hydrogen (Refs. 4, 5). The degree of error is dependent chiefly upon the surface cleanliness of the weld sample, *i.e.*, the presence of an oxide film reduces the rate at which hydrogen is evolved. It is clear that, if accurate measurements of diffusible hydrogen are required, the correct course of action, using room temperature collection, would be to record the column of collected hydrogen only when evolution had ceased. Inevitably, the longer collection time involved, typically 12 to 14 but sometimes as long as 21 days, renders the measurement technique unsuitable for routine use by industry, where both consumable production and on-site fabrication work depend, for practical and economic reasons, upon the rapid classification and approval of consumables.

The economic penalty associated with long collection times has been recognized by the International Institute of Welding (IIW) (Ref. 6) and British Standards Institution (BSI) (Ref. 7), who have developed standards that incorporate the option of using more rapid methods of measurement based upon heating the sample. Similar recognition of the problem is seen in AWS A3.4-86 (Ref. 8), in which diffusible hydrogen is extracted at 45°C (113°F) and collected over mercury, the measurement time being 72 h. This standard also indicates that an extraction time of 6 h at 150°C (302°F) is acceptable, but clearly mercury is not usable at this extraction temperature and other means of measurement, such as gas chromatography, are suggested. While acknowledging the inevitable move toward instrumental techniques, it was

KEY WORDS

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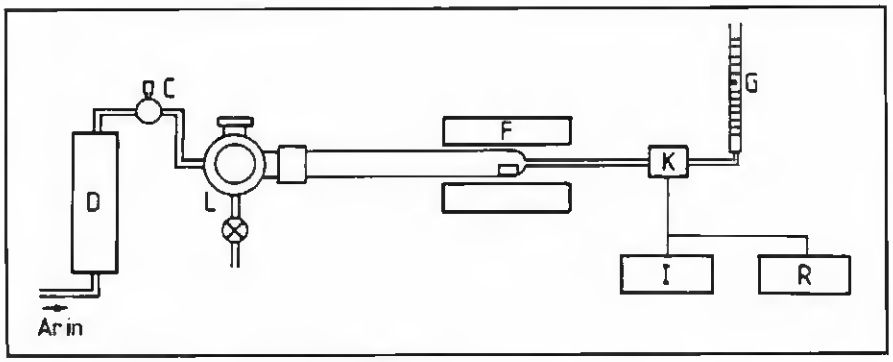

Fig. 1 — Schematic diagram of the carrier gas instrument. D — Molecular sieve drier; C — gas flow controller; L — loading dock; F — furnace; K — katharometer; G — gas flow indicator; I — integrator; R — recorder.

thought essential by IIW to retain the room temperature diffusible hydrogen measurement as a primary reference method. This is in accord with other analytical measurements, which must all be traceable, either directly or indirectly, to a primary method of analysis that is free of bias and can be operated with a known degree of precision.

As indicated above, the total hydrogen present in ferritic steel weld metals at room temperature consists of two fractions first, diffusible hydrogen, which will diffuse freely and evolve from the steel, and second, residual hydrogen which is present in the steel in various ways, e.g., combined, molecular, etc. The traditional temperature for extracting "total" hydrogen from ferritic steel is 650°C (1202°F) (Ref. 9), and at this temperature residual hydrogen is mobilized and measured with the room temperature diffusible hydrogen. Although analysis is rapid, the fact that total hydrogen is measured means that this temperature has not been adopted by the welding industry, which requires a room temperature diffusible hydrogen measurement, arising from concern over the mobile hydrogen content that is involved in cracking at temperatures close to normal ambient.

An inevitable feature of the use of elevated temperatures to obtain rapid results is the release of room temperature residual hydrogen. The temperature at which this release starts will depend upon the nature of the trapping, but at 300°C (572°F), for example, Welding Institute hydrogen standards (Ref. 10) will release significant amounts of hydrogen trapped in molecular form (Refs. 11, 12). This indicates that at 400°C (752°F) most of the room temperature residual hydrogen will be released, if present in molecular form, rather than a compound such as methane. Such considerations are important if temperatures above about 200°C (392°F) are chosen, since the result for hydrogen could be consistently higher than that obtained by extraction at room temperature.

A program is described that investigated the feasibility of employing elevated temperature rapid methods for weld hydrogen analysis. Standard techniques for producing single weld beads, rapidly quenched down to low temperatures, were used, and extraction temperatures in the range of ambient to 400°C were compared against the primary method in conjunction with residual hydrogen measurements determined at 650°C. A range of consumable types and welding processes including SMAW, FCAW and SAW processes has been used.

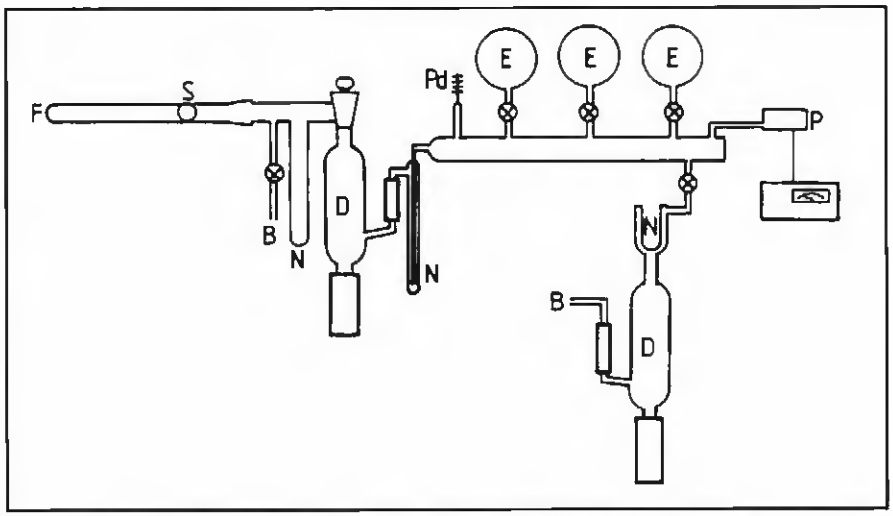

Fig. 2 — Schematic diagram of vacuum hot extraction apparatus. F — furnace tube; S — sample inlet; B — backing line; N — liquid nitrogen cold trap; D — mercury diffusion pump; Pd — palladium tube; E — expansion volume; P — pressure gauge.

Experimental Approach

There were three main areas of investigation. First, diffusible hydrogen recovery was examined at different extraction temperatures to define a suitable extraction temperature in terms of time and consistency of results. This was carried out using one type of SMAW electrode. Second, the effect of surface oxide on hydrogen recovery at different extraction temperatures was studied, again using one SMAW electrode. Finally, a range of welding consumables was tested to determine the effect of varying diffusible/residual hydrogen ratios on whether, and to what extent, residual hydrogen was measured when diffusible hydrogen was extracted at elevated temperatures. In all the series of tests, standard procedures described in BS 6693 were used for producing the weld samples, and for comparison purposes, measurements of diffusible hydrogen were made at ambient temperature by collection over mercury in a Y-tube. Other analysis techniques were the Oerlikon/Yanaco (O/Y) diffusible hydrogen analyzer used at 150°C, a carrier gas (CG) instrument (Fig. 1) used at 300°, 400° and 600°C, and vacuum hot extraction (VHE) equipment (Fig. 2) used at 45°, 150°, 300°, 400° and 650°C.

Experimental Details and Equipment

Test Piece Assemblies and Chemical Composition

Test piece assemblies were prepared from bright mild steel bar stock, which was surface ground to provide cross sections according to the different requirements of BS 6693 appropriate to the different welding processes. The center test pieces were degassed in vacuum at

Table 1 — Chemical Composition of SAW Wires, Welds and Test Piece Material (wt-%)

Sample	Element (wt-%)												
	C	S	P	Si	Mn	Ni	Cr	Mo	V	Cu	Ti	Al	B
SMAW													
E7018-1	0.11	0.12	0.010	0.37	1.30	0.07	0.05	0.01	0.01	0.11	0.006	0.005	<0.0003
E7028, Brand A	0.11	0.011	0.019	0.30	0.98	0.02	0.02	<0.005	0.01	0.02	<0.002	0.003	<0.0003
E7028, Brand B	0.12	0.09	0.022	0.31	0.96	0.07	0.10	0.01	0.002	0.17	<0.002	0.003	<0.0003
E9018	0.10	0.008	0.019	0.32	1.09	0.50	0.07	0.17	0.01	0.17	0.005	0.004	<0.0003
E12018	0.11	0.018	0.015	0.34	1.27	1.25	0.33	0.26	0.01	0.17	0.005	0.003	<0.0003
FCAW													
Metal cored C-Mn	0.09	0.011	0.011	0.37	1.32	0.02	0.01	0.005	0.005	0.005	0.006	0.005	0.0018
Metal cored low-alloy	0.10	0.014	0.014	0.34	1.26	1.37	0.02	0.39	0.005	0.01	0.003	0.008	<0.0003
E70T-1	0.09	0.021	0.016	0.56	1.36	0.07	0.08	0.02	0.01	0.12	0.025	0.011	0.0004
E71T-7	0.16	0.008	0.012	0.16	0.79	0.07	0.05	0.02	0.005	0.12	0.005	0.74	0.0007
Self-shielded low-alloy	0.10	0.007	0.014	0.25	1.01	0.62	0.07	0.02	<0.002	0.18	<0.002	0.42	<0.0003
Gas shielded low-alloy	0.11	0.024	0.015	0.30	1.10	1.02	0.07	0.21	0.01	0.16	0.027	<0.003	0.0034
SAW													
Basic Flux A, low-alloy cored wire	0.13	0.007	0.015	0.25	0.99	1.08	0.23	0.23	0.02	0.03	<0.002	0.013	0.0005
Basic Flux A, C-Mo wire	0.13	0.007	0.017	0.35	0.79	0.02	0.03	0.19	0.02	0.03	0.033	0.010	0.0009
Basic Flux B, C-Mn wire	0.14	0.015	0.015	0.29	1.09	0.08	0.06	0.01	0.002	0.22	<0.002	0.017	<0.0003
Basic Flux C, low-alloy wire	0.13	0.012	0.015	0.29	1.05	0.86	0.15	0.17	<0.002	0.12	0.003	0.017	<0.0003
Typical base plate	0.19	0.021	0.016	0.20	0.74	0.03	0.04	0.005	<0.002	0.06	<0.002	0.005	<0.0003

700°C (1292°F) for one hour and weighed before welding. The test piece material, submerged arc welding wire and test welds were analyzed by use of optical emission spectrometry, and the results are given in Table 1.

Welding

General

All welding was by mechanized deposition except for the E7028 Brand A consumable. SMA welding was carried out using custom-built equipment providing mechanized deposition of covered electrodes.

All welded samples were stored in liquid nitrogen after welding until required for analysis. For each series of welds involving comparisons between analysis methods and hydrogen extraction temperatures, welding was completed during the course of one day.

Shielded Metal Arc Welds

For the initial study, over a range of extraction temperatures, 4-mm (5/32-in.) E7018-1 electrodes were used, which were supplied in a partially dried condition to allow selection of a drying temperature to give 10 mL/100 g of deposited metal diffusible hydrogen. After initial tests the selected drying condition was 2 h at 300°C. Because large batches of electrodes were required for each series of welds, which had to be completed in one day, a number of electrodes were dried and sealed in lots of five or six in glass tubes. Using this technique, each series of welds could be completed within a 7-h period, breaking open the glass tube only when ready to weld, thereby using the electrodes within a 30-min period. The welding was carried out using DC electrode positive with average parameters of 170 A and 21.5 V.

Low-alloy electrodes E12018 (4 mm in diameter) for use in the later part of the study were also obtained in a partially dried condition and similarly dried for 2 h at 300°C to give weld hydrogen levels of approximately 10 mL/100 g of deposited metal (H_{DM}). Similar welding parameters were adopted.

Three further SMAW electrodes were used in the later study, and these are described in Table 2 together with the welding conditions used. For all the SMAW deposits, travel speed was adjusted to give a deposit weight of 4 g, and this was generally achieved.

Flux Cored Wire Welds

Four different cored electrodes were used, and these are described, together with the welding parameters, in Table 2. In each case the travel speed in the mechanized welding was selected to give about 4 g of deposit on the 30-mm (1.2-in.) length of test weld.

Submerged Arc Welds

Submerged arc test welds were made following BS 6693 Part 4 and using a heat input of 3 kJ/mm (76 kJ/in.) for the consumables and welding conditions given in Table 2. Flux A was used after drying for 1 h at 275°C (527°F), while flux B, supplied in a nonstandard partially dried condition, was dried at 150°C (302°F) for 18 h to give about 10 mL H_{DM}. Flux C was used in the as-received condition.

Analysis of the Test Welds for Diffusible and Residual Hydrogen

Collection over Mercury Using Y-Tubes

The welds were analyzed at ambient temperature (approximately 20°C) by extraction of the diffusible hydrogen in a Y-tube with collection over mercury. Sample preparation and method of operation followed standard descriptions as in BS 6693 and ISO 3690 except for one series of E7018 deposits, which was left in the as-welded condition to study the effect of surface oxide. Hydrogen evolved was measured at intervals until discernible evolution ceased. After the final measurement, the samples were removed from the Y-tube and stored in liquid nitrogen until residual hydrogen measurements at 650°C were carried out.

Carrier Gas Measurements

The principle for carrier gas extraction of hydrogen from weld specimens involves heating the specimen in a controlled flow of dried high-purity argon and the use of a thermal conductivity detector to monitor the release of hydrogen. A schematic diagram of the TWI-built equipment is shown in Fig.1. The TWI-built instrument allows the sample to be heated in a constant flow of "dry" argon at about 100 mL/min. Evolved hydrogen

Table 2 — Consumables and Welding Parameters

Consumable	Current, A ± 1σ	Voltage V ± 1σ	Polarity	Wire feed speed m/min	Arc time for 100mm weld sec ± 1σ	stickout, mm	% RH during welding
SMAW							
E7028, Brand A 3.2 mm	130 ± 4	25 ± 2	AC	na	36 ± 1	na	56% at 24°C
E7028, Brand B 3.2 mm	153 ± 1	32 ± 3	DC + ve	na	26 ± 1	na	55% at 21° C
E9018 4 mm	170 ± 1	21 ± 1	DC + ve	na	34 ± 1	na	46% at 23°C
Cored wires							
Metal cored C-Mn 1.2 mm	223 ± 6	27 ± 1	DC + ve	6.7	17 ± 1	15	54% at 25°C
Metal cored low-alloy 1.2 mm	224 ± 5	27 ± 0.5	DC + ve	6.7	21 ± 1	15	49% at 22°C
E70T-1, 1.6 mm	224 ± 4	23.4 ± 4	DC + ve	4.7	15 ± 0.5	25	49% at 22.5°C
E71T-7, 1.6 mm	227 ± 5	23.7 ± 0.2	DC + ve	4.1	20 ± 3.0	25	49% at 22.5°C
Self-shielded, low-alloy 2.0 mm	194 ± 3	18.6 ± 0.1	DC + ve	1.7	30 ± 0.7	25	48% at 17°C
Gas shielded, low-alloy 1.6 mm	271 ± 2	28.2 ± 0.1	DC + ve	5.2	14 ± 0.5	25	49% at 17°C
SAW							
Basic flux A, low-alloy cored wire	605 ± 8	30	DC + ve	nm	36 ± 1[a]	30	47% at 17°C
Basic flux A, with C-Mo solid wire	648 ± 11	30	DC + ve	nm	36 ± 1[a]	30	72% at 19°C
Basic flux B with solid C-Mn wire	649 ± 5	32.2 ± 0.1	DC + ve	nm	31 ± 1.4[a]	30	65% at 16.55°C
Basic flux C with low-alloy wire	656 ± 3	32.2 ± 0.3	DC + ve	nm	29 ± 0.6[a]	35	64% at 16.5°C

na = not applicable.
a = laid manually.
nm = not measured.
Gas shield for FCAW 85%Ar/15%CO_2 at 20 L/min.

is monitored by the detector whose output traces a peak on a recorder, the area of the peak being proportional to the volume of the hydrogen that has evolved. Cleaning the samples and bringing them to ambient temperature are achieved in a similar manner to that for samples being analyzed using mercury and Y-tubes. To raise the sample to the analysis temperature as rapidly as possible, the heating furnace was given a predetermined excess setting, which was lowered to the required temperature as the sample temperature rose. Welding Institute hydrogen standards consist of molecular hydrogen sealed at a known temperature and pressure in a steel cylinder of precisely known internal volume. By heating the standard, for example to 650°C, the hydrogen disassociates and is quantitatively released through the walls of the cylinder (Ref. 10). The instrument is linear over the full range of Welding Institute hydrogen standards and was calibrated at 650°C using size H5 hydrogen standards containing 0.575mL of hydrogen at STP.

Table 3 — E7018 Electrode, Means of Analyses at Each Temperature

Analysis Method	Hydrogen, mL/100g Deposited Metal H_{DM}	Residual	Total
Y-tube	10.1	0.45	10.6
VHE 45°C	10.8	0.49	11.3
VHE 150°	10.4	0.42	10.8
O/Y 150°C	10.1	0.40	10.5
VHE 300°C	9.88	0.33	10.2
CG 300°C	9.99	0.42	10.4
VHE 400°C	9.81	0.40	10.2
CG 400°C	10.7	0.43	11.1
VHE 650°C	10.6	—	10.6
CG 650°C	11.5	—	11.5

After measurement of hydrogen, the samples were cooled down in the argon carrier to avoid oxidation and then transferred to liquid nitrogen for storage until residual hydrogen could subsequently be measured by VHE at 650°C. Analysis of diffusible hydrogen was carried out at temperatures of 300°, 400° and 650°C.

Vacuum Hot Extraction Measurements

A schematic diagram of the TWI-built equipment, which is of glass construction with a transparent silica furnace tube, is shown in Fig. 2. While the sample was maintained at the chosen extraction temperature in the furnace, evolved hydrogen was transferred to the analysis volume together with any other gases emitted from the sample or furnace tube. Condensible gases were frozen out in a liquid nitrogen cold trap in both the furnace section and the analysis volume. Total pressure was monitored continuously by use of a Baratron pressure gauge and recorded. When hydrogen evolution ceased, the total pressure was noted. Hydrogen was then removed from the analysis volume through the palladium/silver osmosis tube, and the pressure of residual gases was noted. The difference in pressure was the partial pressure of the hydrogen extracted from the sample. The temperature of each sample, which was loaded cold into the furnace tube, was monitored during analysis by means of an attached degassed chromel/alumel thermocouple. Residual hydrogen was measured using the VHE at 650°C on all samples by raising the sample to this temperature as quickly as possible from the previous extraction temperature and so completing the hydrogen removal. Oxidized samples were cleaned by wire brushing before analysis at 650°C.

The analysis of samples at 45°C could not be completed within 8 h. It was anticipated that 72 h would be required for complete extraction of the diffusible hydrogen, as indicated in the AWS standard. The technique adopted was to leave the sample overnight in the fur-

nace tube at 45°C, with the cold trap filled with liquid nitrogen, but with the furnace isolated from the analysis volume by the glass stopcock. Each morning, the equipment was switched on, the gases in the furnace section transferred to the analysis volume and analyzed for hydrogen. Similar measurements were taken during the day, and all readings were summed when evolution was judged to have ceased.

Oerlikon/Yanaco Measurement

The O/Y hydrogen analyzer Model G-1006 was included in the analysis techniques in the program of work to allow the analysis of samples at 150°C, which is an optional temperature specified in the AWS standard. Although the O/Y analyzer uses a static collection and measurement technique, as compared with the dynamic integrating technique of the CG instrument, both methods use thermal conductivity measurements and, given accurate calibration, should yield the same analysis results on equivalent samples. Preparation of the samples before introduction into the analyzer followed the same procedures as for the other analysis techniques.

Results and Discussion

Effect of Analysis Temperature upon Results and Extraction Time (E7108 Electrode)

Table 3 gives the mean of three analyses at each of the temperatures studied together with the subsequent residual hydrogen measured at 650°C for 0.5 h. The recorded times for complete evolution of diffusible hydrogen using the VHE equipment were 48 h at 45°C, up to 150 min at 150°C, 50 min at 300°C and 30 min at 400°C. These were times at temperature, and obviously full analysis times would be longer when an allowance for heating time is included. For temperatures up to and including 400°C, the VHE results suggest that for this consumable no significant extraction of residual hydrogen took place.

The carrier gas results at 650° and possibly even those at 400° are above the VHE results. The reason for this is believed to be associated with traces of moisture in the argon carrier. Any traces of moisture in the argon carrier will react with the sample surface to produce iron oxide and release hydrogen. Surface oxide could often be seen on the end of the sample that faced the argon flow. The amount of hydrogen released at 400°C appeared to be very low, but at 650°C it was usually observed to be slightly higher and more variable. This was supported by the recorder traces of hydrogen evolution as a function of time, which at 400° and more particularly at 650°C did

Table 4 — Comparison of Diffusible Hydrogen of Cleaned and As-Welded E7018-1 SMAW Welds Analyzed by Different Methods Using Student t Test

Analysis Method	Y-tube	CG 300°C	CG 400°C	VHE 400°C
(1) Cleaned. Y-tube vs. method of analysis				
Mean	10.2	10.6	11.2	11.1
Std dev	0.28	0.40	0.52	0.33
Number	4	4	4	4
D of F	—	6	6	6
t	—	−1.833	−3.312	−4.261
Significance	—	NS	S	S
(2) As-welded. Y-tube vs. method of analysis				
Mean	10.2	10.1	10.4	9.84
Std dev	0.28	0.17	0.07	0.43
Number	4	4	4	4
D of F	—	6	6	6
t	—	0.415	−1.399	1.387
Significance	—	NS	NS	NS
(3) As-welded vs. cleaned for each analysis method				
t		−2.348	2.609	4.673
Significance		NS	S	S

Table 5 — Mean Diffusible and Residual Hydrogen Results (mL/100 g deposited metal)

	Analysis method								
	Y-tube			O/Y 150°C			VHE 400°C		
Consumable	Diffusible	Residual	Total	Diffusible	Residual	Total	Diffusible	Residual	Total
SMAW									
E7028 (A) 3.2 mm	3.22	0.40	3.61	3.11	0.34	3.45	3.64	0.47	4.11
E7028 (B) 3.2 mm	3.59	0.29	3.88	3.69	0.33	4.01	4.42	0.43	4.85
E9018, 4.0 mm	3.34	0.44	3.78	3.23	0.33	3.55	3.82	0.34	4.16
E12018 4.0 mm	10.7	0.67	11.4	ND	ND	ND	10.9	0.42	11.3
FCAW									
Metal cored, C-Mn 1.2 mm	1.44	0.35	1.78	1.51	0.33	1.83	1.65	0.34	1.99
Metal cored, low-alloy	2.96	0.60	3.55	3.21	0.31	3.51	3.28	0.44	3.72
E70T-1, 1.6 mm	3.72	0.65	4.37	ND	ND	ND	4.71	0.47	5.18
E70T-7, 1.6 mm	10.3	3.97	14.3	ND	ND	ND	14.1	0.95	15.1
Self-shielded, low-alloy, 2.0 mm	7.29	0.94	8.23	7.32	0.67	7.99	8.12	0.50	8.62
Gas shielded, low-alloy 1.6 mm	12.4	0.73	13.1	12.7	0.59	13.3	13.7	0.46	14.3
SAW									
Basic flux A with 4 mm low-alloy cored wire	2.93	0.84	3.94	2.99	0.46	3.45	3.58	0.44	4.02
Basic flux A with 4 mm solid C-Mo wire	3.30	0.75	4.05	4.12	0.56	4.67	4.74	0.46	5.20
Basic flux B with solid C-Mn wire	9.73	0.64	10.4	ND	ND	ND	11.1	0.48	11.6
Basic flux C with 4 mm solid low-alloy wire	7.22	0.59	7.81	7.75	0.46	8.21	8.33	0.34	8.67

ND — not determined.

Table 6 — Comparison of Means of Diffusible Hydrogen Results on Welds Analyzed by Different Methods

		Y-tube	O/Y 150°C	VHE 400°C
SMAW				
E7028 (A), 3.2 mm	Mean	3.3	3.11	3.64
	Std dev	0.21	0.24	0.25
	Number	6	6	6
	D of F	—	10	10
	t	—	0.809	−3.193
	Significance	—	NS	S
E7028 (B), 3.2 mm	Mean	3.59	3.69	4.42
	Std dev	0.38	0.50	0.50
	Number	6	6	6
	D of F	—	10	10
	t	—	−0.391	−3.233
	Significance	—	NS	S
E9018, 4.0 mm	Mean	3.34	3.29	3.82
	Std dev	0.16	0.20	0.12
	Number	6	6	6
	D of F	—	10	10
	t	—	1.108	−5.934
	Significance	—	NS	S
E7018, 4.0 mm	Mean	10.2	10.8	11.1
	σ	0.28	0.38	0.33
	Number	4	4	4
	D of F	—	6	6
	t	—	−2.591	−4.261
	Significance	—	S	S
E12018, 4.0 mm	Mean	10.7	—	11.0
	σ	0.15	—	0.24
	Number	6	—	6
	D of F	—	—	10
	t	—	—	−2.049
	Significance	—	—	NS
FCAW				
Metal cored, C-Mn 1.2 mm	Mean	1.44	1.51	1.65
	Std dev	0.46	0.52	0.38
	Number	6	6	6
	D of F	—	10	10
	t	—	−0.248	−0.852
	Significance	—	NS	NS
Metal cored, Low-alloy	Mean	2.96	3.20	3.28
	Std dev	0.97	0.60	0.72
	Number	6	6	6
	D of F	—	10	10
	t	—	−0.535	−0.663
	Significance	—	NS	NS
E70T-1, 1.6 mm	Mean	3.72	—	4.71
	Std dev	0.72	—	0.47
	Number	6	—	6
	D of F	—	—	10
	t	—	—	−2.7944
	Significance	—	—	S
E70T-7 1.6 mm	Mean	10.3	—	14.1
	σ	0.63	—	0.84
	Number	6	—	6
	D of F	—	—	10
	t	—	—	−8.933
	Significance	—	—	S

not return to zero after the bulk of evolution had taken place. This reaction of carrier gas moisture is potentially a major drawback for carrier gas methods at elevated temperatures. Ideally, the carrier should be dried to zero moisture content, although this is practically impossible. If, on removal of a sample from the analysis furnace an oxide film is observed extending along the sample, then this is a sure indication that the carrier gas contained excessive moisture and that high results should be expected.

The above comments also apply to reactions between any moisture in the argon carrier and the standard used to calibrate the carrier gas instrument. It should be noted that any inaccuracies from this effect are to some extent calibrated out because the calibration procedure exactly reproduces the analysis technique. Carrier drying techniques used within the instrument reduce the moisture content to as low a level as possible and prevent variations that might otherwise occur due to varying gas cylinder pressure.

The residual hydrogen measurements, also shown in Table 3, were typically low, and there was no trend for them to decrease as the diffusible analysis temperature was raised to 400°C. It can be seen from the results in Table 3 that diffusible hydrogen levels measured by VHE at temperatures of 150°, 300° and 400°C were very close to the primary method value of 10.1 mL/100 g. The subsequent testing was done to explore the extent to which this preliminary finding, that diffusible hydrogen could be measured at up to 400°C without the risk of obtaining a high result due to release of residual hydrogen, applied to a range of other consumables.

The Effect of Surface Oxide on Diffusible Hydrogen Measurements Made at Elevated Temperatures

These tests were carried out on the same E7108 consumable, and the results are given in Table 4. Both the VHE and CG methods gave lower results for diffusible hydrogen at 400°C from as-welded samples than from samples for which the surface oxide had been removed. The difference was not large, 0.73 mL/100 g for CG and 1.26 mL/100 g for VHE. Although the loss of hydrogen by oxidation to water as it passes through the heated oxide on the weld surface is small, these tests demonstrate that for the samples analyzed by heating to 400°C stringent cleaning of the weld is required if low results are to be avoided. A possible explanation for the higher loss by VHE is the more rapid heating rate experienced by samples analyzed by this technique, thus giving a longer time at higher temperature. This finding on the reaction of hydrogen with a surface oxide is in agreement with a previous study reported by Jenkins and Greenfield (Ref. 11) who based their investigation on the analysis of oxidized hydrogen standards. However, at 300°C the results show that the presence of surface oxide during analysis did not significantly reduce the measured hydrogen.

Behavior of Other Consumables

The hydrogen analysis results, given as means, generally of six tests, are presented in Table 5. Overall, it can be seen that the results from extraction at 150°C

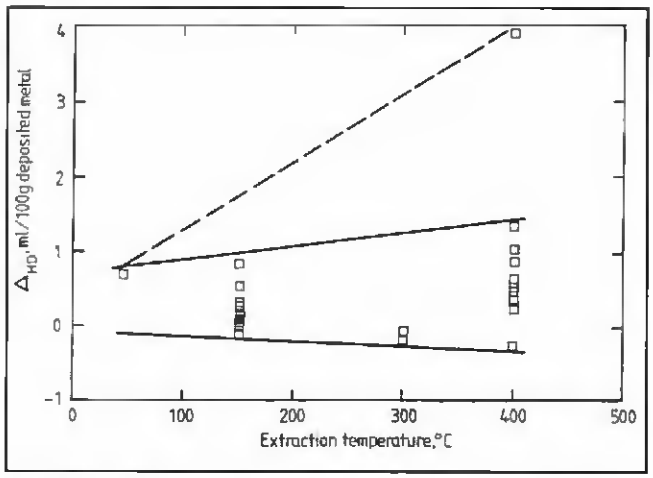

Fig. 3 — The difference, Δ_{HD}, in diffusible hydrogen content between the primary and elevated temperature methods, expressed as a function of extraction temperature.

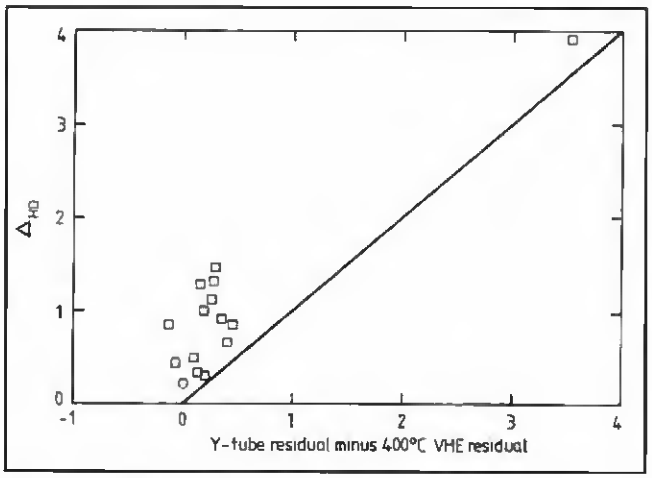

Fig. 4 — Comparison of the difference, Δ_{HD}, in diffusible hydrogen content between the 400°C VHE and the Y-tube methods with the difference in residual hydrogen in the Y-tube and 400°C VHE samples, as mL/100 g.

agree very well with the Y-tube results. At the 400°C extraction temperature there is also, generally, good agreement, although there was one notable exception for a carbon-manganese self-shielded consumable that was observed to contain some subsurface porosity — Fig. 3. The deposits from this consumable had variable Y-tube residuals of up to 5.7 mL hydrogen/100 g (*i.e.*, nearly 60% of the total), and nearly 90% of this residual hydrogen was released at 400°C leading to a serious error in the results.

Close examination of Table 5 shows that the 400°C VHE diffusible hydrogen was always slightly higher than the Y-tube value. A statistical comparison of means to detect the significance of differences at the 5% level was carried out using the student t test, and the results are given in Table 6 for diffusible and Table 7 for residual hydrogen data. The t test data indicate that the majority of the 150°C results were not significantly different from the Y-tube values. In contrast, the t test indicates that the majority of the differences between 400°C VHE and Y-tube results were statistically significant at the 5% level. However, it is also true that these differences were small and generally within the ±10% reproducibility of the method previously reported at the 10 mL/100 g hydrogen level (Ref. 13). If the 400°C VHE values were higher just due to the release of residual hydrogen, then the increase over the Y-tube diffusible value should equal the differences between Y-tube and 400°C VHE residuals. Table 8 and Fig. 4 compare these differences and show that, in all cases, the increase in the 400°C VHE results slightly exceeds the difference in residuals. This indicates that there was a method bias in the 400°C VHE results. A probable cause of this is that the VHE samples were always loaded cold from liquid nitrogen storage, while the Y-tube samples were always allowed to warm to room temperature, thereby losing some hydrogen before analysis. Moreover, it can be seen that, with the exception of

Table 6 — Continued

Self-shielded low-alloy 2.0 mm	Mean	7.29	7.32	8.12
	σ	0.25	0.10	0.49
	Number	6	6	6
	D of F	—	10	10
	t	—	−0.215	−3.702
	Significance	—	NS	S
Gas shielded, low-alloy, 1.6 mm	Mean	12.4	12.7	13.7
	σ	1.19	0.94	0.68
	Number	6	6	6
	D of F	—	10	10
	t	—	−0.380	−2.207
	Significance	—	NS	NS
SAW				
Basic flux A with 4-mm low-alloy cored wire	Mean	2.93	2.99	3.58
	Std dev	0.36	0.47	0.32
	Number	6	6	6
	D of F	—	10	10
	t	—	−0.260	−3.338
	Significance	—	NS	S
Basic flux A with 4-mm solid C-Mo wire	Mean	3.30	4.12	4.74
	Std dev	0.32	0.38	0.39
	Number	6	6	6
	D of F	—	10	10
	t	—	−3.991	−7.106
	Significance	—	S	S
Basic flux B with solid C-mm wire	Mean	9.73	—	11.1
	Std dev	0.67	—	0.51
	Number	6	—	6
	D of F	—	—	10
	t	—	—	−3.859
	Significance	—	—	S
Basic flux C 4-mm solid low-alloy wire	Mean	7.22	7.75	8.33
	σ	0.23	0.49	0.60
	Number	6	6	6
	D of F	—	10	10
	t	—	−2.371	−4.245
	Significance	—	S	S

Hydrogen means, mL/100 g deposited metal.
S Difference significant at 5% level.
NS Difference not significant at 5% level.

Table 7 — Comparison of Means of Residual Hydrogen Results Determined by VHE at 650°C on Welds Previously Analyzed for Diffusible Hydrogen by Different Methods

SMAW		Y-tube	O/Y 150°C	VHE 400°C
E7028 (A), 3.2 mm	Mean	0.40	0.34	0.47
	Std dev	0.09	0.05	0.06
	Number	6	6	6
	D of F	—	10	10
	t	—	1.425	−1.513
	Significance	—	NS	NS
E7028 (B), 3.2 mm	Mean	0.29	0.33	0.43
	Std dev	0.08	0.05	0.08
	Number	6	6	6
	D of F	—	10	10
	t	—	−1.024	−3.238
	Significance	—	NS	S
E9018, 4 mm	Mean	0.44	0.33	0.34
	Std dev	0.08	0.05	0.04
	Number	6	6	6
	D of F	—	10	10
	t	—	2.893	2.566
	Significance	—	S	S
E7018, 4 mm	Mean	0.74	1.16	0.38
	σ	0.18	0.17	0.08
	Number	4	4	4
	D of F	—	6	6
	t		−3.422	3.679
	Significance	—	S	S
E12018, 4 mm	Mean	0.67	—	0.42
	σ	0.12	—	0.04
	Number	6	—	6
	D of F	—	—	10
	t	—	—	4.498
	Significance	—	—	S
FCAW				
Metal-cored, C-mn, 1.2 mm	Mean	0.35	0.33	0.34
	Std dev	0.04	0.04	0.09
	Number	6	6	6
	D of F	—	10	10
	t	—	0.917	0.165
	Significance	—	NS	NS
Metal cored, Low-alloy	Mean	0.60	0.31	0.44
	Std dev	0.10	0.06	0.09
	Number	6	6	6
	D of F	—	10	10
	t	—	5.850	2.737
	Significance	—	S	S
E70T-1, 1.6 mm	Mean	0.65	—	0.47
	Std dev	0.02	—	0.05
	Number	6	—	6
	D of F	—	—	10
	t	—	—	5.768
	Significance	—	—	S
E70T-7, 1.6 mm	Mean	3.97	—	0.45
	σ	0.63	—	0.18
	Number	6	—	6
	D of F	—	—	10
	t	—	—	7.223
	Significance	—	—	S
Self-shielded low-alloy, 2 mm	Mean	0.94	0.67	0.50
	σ	0.16	0.11	0.06
	Number	6	6	6
	D of F	—	10	10
	t	—	3.489	6.500
	Significance	—	S	S

the weld containing porosity, the maximum difference between the two residual hydrogen values, *i.e.*, the amount released, was 0.44 mL/100 g and is small.

In selecting the welding processes and consumables used for this part of the study, the aim was to cover a range of alloy content, consumable type and microstructure, so as to detect any effect these differences had on the amount of residual hydrogen and its propensity for release at the elevated extraction temperatures. However, because the residual hydrogen content was considerably less than 1 mL/100 g (with the exception of the porous weld), the amount released at elevated temperatures was small, as mentioned above. There was a general trend for residual hydrogen to decrease with increasing diffusible hydrogen analysis temperature, but the statistical examination of the results was unable to attribute the effect to a particular alloy type. At the same time, the effect appeared to be strongest with the cored wire and submerged arc processes, where the proportion of the hydrogen present in the residual form was highest. Thus, for the wide range of consumables tested, the results indicate that a small amount of residual hydrogen is released when diffusible hydrogen is extracted at elevated temperatures of 150° to 400°C, the amount being greater at the higher temperatures. However, the amount is small, and within the wide range of consumable types and compositions studied, with the exception of welds containing porosity, it was not possible to identify any particular weld metal type that would lead to serious errors during diffusible hydrogen measurement at temperatures up to 400°C. One trend with composition was noted, and that was for analysis time at 400°C to increase to ~40 min for the low-alloy deposit, presumably as a result of slightly reduced diffusion rates.

Practical Implications

The present results show clearly that analysis times for diffusible hydrogen can be very dramatically reduced by the adoption of elevated temperature extraction techniques. Analysis times can be reduced from 14 to 21 days for the primary method over mercury at normal ambient temperatures, to around 30 min at 400°C. There was some indication that the low-alloy deposits had a lower diffusivity and that this may increase the time at 400°C to about 40 min. However, the study has also shown that, as the temperature of analysis is raised, and particularly as 400°C is approached, the opportunity increases for errors to be introduced.

Three main sources of error have been highlighted. First of all, for carrier gas techniques there is a potential risk of higher values being recorded due to reduction of any water in the carrier gas. In practice, this error is likely to be small and could be spotted by observing the pres-

ence of oxide on the analyzed sample. Secondly, if samples for analysis are not properly cleaned and contain surface oxides, low diffusible hydrogen results may be produced because of oxidation of the hydrogen to water on passing through the surface oxides. The solution to this problem is to ensure that samples are thoroughly wire brushed before analysis at 400°C. Finally, there is the error associated with the release of residual hydrogen at the elevated extraction temperatures. Certainly at temperatures of up to 150°C, there was generally good agreement with Y-tube results and there were only very small indications of movement of residual hydrogen. Even at 400°C, there was also satisfactory agreement with Y-tube results, although the amount of residual hydrogen released was greater at this higher temperature. However, because, with one exception, the residual hydrogen levels were low, the amount released at 400°C was also low, the maximum amount being 0.44 mL/100 g. The exception to this generally acceptable picture, and that giving the greatest inaccuracy, occurred for a self-shielded FCA weld deposit that contained subsurface porosity. In this case, not only was the residual hydrogen level very high (up to 5.7 mL/100 g), but at 400°C, nearly 90% of this was released. This demonstrates the importance, for all weld hydrogen measurements, of ensuring that sound weld deposits are produced.

With the exception of the error due to the presence of surface oxides, the other errors would produce results that were conservative from a hydrogen cracking risk point of view. Moreover, in general, the residual hydrogen levels were observed to decrease as the diffusible hydrogen levels decreased. Thus, with the general trend for weld hydrogen levels of modern consumables to attain lower values, any errors in the use of elevated temperature techniques due to release of residual hydrogen are also likely to decrease.

Although it was not the aim of this work to study the reproducibility of the different methods, it is apparent from Table 6, when looking at the diffusible hydrogen results, that for each consumable, there is a reasonably close agreement between the standard deviations for each method. However, there does appear to be a wider variation in standard deviation between consumables and processes. This strongly suggests that the poor reproducibility often exhibited by diffusible hydrogen results is probably more a feature of variability arising from the welding process and consumable than from the analytical method.

Table 7 — Continued

Gas-shielded, low-alloy, 1.6 mm	Mean	0.73	0.59	0.46
	σ	0.06	0.06	0.06
	Number	6	6	6
	D of F	—	10	10
	t	—	4.116	8.440
	Significance	—	S	S
SAW				
Basic flux A with 4-mm low-alloy cored wire	Mean	0.84	0.46	0.44
	Std dev	0.07	0.09	0.12
	Number	6	6	6
	D of F	—	10	10
	t	—	8.389	7.139
	Significance	—	S	S
Basic flux A with 4-mm solid C-Mo wire	Mean	0.75	0.56	0.46
	Std dev	0.07	0.09	0.17
	Number	6	6	6
	D of F	—	10	10
	t	—	4.237	3.899
	Significance	—	S	S
Basic flux B with solid C-Mn wire	Mean	0.64	—	0.48
	Std dev	0.05	—	0.12
	Number	6	—	6
	D of F	—	—	10
	t	—	—	2.909
	Significance	—	—	S
Basic flux C 4-mm solid low-alloy wire	Mean	0.59	0.46	0.34
	σ	0.07	0.07	0.06
	Number	6	6	6
	D of F	—	10	10
	t	—	3.306	6.391
	Significance	—	S	S

Hydrogen means mL/100 g deposited metal.
S Difference significant at 5% level.
NS Difference not significant at 5% level.

Conclusions

Measurements have been made of both diffusible and residual hydrogen levels in a range of hydrogen-controlled SMAW, FCAW and SAW consumables using different analytical techniques to determine the extent to which elevated temperature extraction methods may be applied. The following conclusions can be made:

1) The use of elevated temperature extraction techniques produces major reductions in analysis time: from the typical 14–21 days for the primary mercury method to approximately 30 min at 400°C.

2) The amount of residual hydrogen released increased with increasing extraction temperature. With one exception, however, the amount was sufficiently small (less than 0.5 mL/100 g) that satisfactory agreement with the primary method was obtained for temperatures up to 400°C.

3) Care must be taken to avoid analyzing welds with subsurface porosity because they will have a high residual hydrogen fraction that could be released at 400°C, giving rise to major errors.

4) Weld samples containing surface oxides will give low results when analyzed at 300° or 400°C because of oxidation of hydrogen. Hence, all samples must be fully cleaned by wire brushing before analysis at these temperatures.

5) When using carrier gas techniques, traces of moisture in the carrier can give small errors due to sample oxidation and the consequent production of hydrogen.

6) With the exception of the porous

Table 8 — Comparison of 400°C VHE & Y-Tube Diffusible and Residual Differences

	Diffusible	Residual
Consumable	400° VHE-Y Tube	Y Tube-400°C VHE
SMAW		
E9018	0.90	0.36
E7028(A)	0.43	−0.07
E7028(B)	0.83	−0.14
E9018	0.48	0.10
E12018	0.30	0.22
FCAW		
Metal Cored, C-Mn	0.21	0.01
Metal Cored, low-alloy	0.32	0.16
E70T-1	0.99	0.18
E71T-7	3.9	3.52
Self-shielded, low-alloy	0.83	0.44
Gas shielded, low-alloy	1.3	0.27
SAW		
Basic Flux A, low-alloy	0.65	0.40
Basic Flux A, C-Mo	1.44	0.29
Basic Flux B, C-Mn	1.28	0.16
Basic Flux C, low-alloy	1.11	0.25

weld, no clear trend for the release of residual hydrogen to be related to consumable type or composition was seen. However, the residual hydrogen fraction appeared to be greater in the flux cored and submerged arc weld deposits, giving a greater risk of significant error.

7) The standard deviations of the diffusible hydrogen results for each consumable were generally consistent for the three analysis methods but showed large variations between consumables. This indicates that the relatively poor reproducibility often exhibited by diffusible hydrogen analysis is probably a feature of the welding process and consumable, rather than the analytical method, which is relatively precise.

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