Determination of the diffusible hydrogen in welds

As a result of the harmful influence of hydrogen on the mechanical properties of metals (e.g. due to embrittlement and to the formation of cracks or pores), great significance is attached to knowing the hydrogen content in such materials not only for the process control and the product quality but also for the development of new materials.

Hydrogen is the lightest element in the periodic system and has the smallest atom diameter. Because of its small size, the hydrogen atom can easily penetrate into a metal lattice. The great mobility there may, in the most diverse forms, lead to damage in and on the components. The best-known negative effects and damage are flake formation, pickling blisters and hydrogen-caused brittle fracture.

Hydrogen can penetrate into the metal during various manufacturing processes, e.g. not only during melting, pickling and annealing but also when the components are utilised due to corrosion. Moreover, atomic hydrogen always builds up in tensile stress regions of the workpiece.

In this connection, hydrogen-caused damage is a widespread phenomenon. Sometimes even without any visible signs of a corrosion attack, components may fail unexpectedly under the influence of stresses.

In particular, higher-strength and high-strength steels with a low alloying proportion have an inclination to this form of hydrogen-induced stress cracking corrosion which is generally also designated as hydrogen embrittlement and in which the crack growth is accelerated by local embrittlement in the region of the crack tip.

However, those irregularities in the lattice and in the structure of the material which are designated as traps are considerably more attractive positions for the absorbed hydrogen because they are more favourable positions with regard to energy than the interstitial positions. Sufficiently large imperfections such as pores and shrinkage cavities may cause the hydrogen accumulating there to recombine into molecular hydrogen gas once again. The volume leap arising in this case may build up pressures of as much as 1,000bar in the interior of the imperfection. This may cause cold cracks in the material which, due to the relatively slow diffusion of the hydrogen at room temperatures, even occur after a lengthy duration.

Cold cracks in welds and welded joints may be caused by hydrogen which penetrates into the material during the welding process. The hydrogen primarily results from the moisture which is present in the material, in the ambient air, in the filler material or as condensation water close to the welding zone.

During the welding (i.e. not only in all the processes in which covered stick electrodes are utilised but also in submerged arc welding), hydrogen from the filler materials may enter the weld pool.

Bruker Elemental is a manufacturer of optical emission spectrometers for metal analysis and of CS/ONH analysis devices for the quick determination of carbon, sulphur, oxygen, nitrogen and hydrogen in different materials. Another product area relates to hand-held XRF devices for quick material recognition. As a subsidiary of Bruker AXS GmbH, Bruker Elemental with its headquarters in Kalkar belongs to the Bruker group.

Fig. 1. *The "G4 Phoenix DH" analyser for the determination of diffusible hydrogen.*

Fig. 2. *Quartz tube for heating up the sample material, with a diameter of 30 mm.*

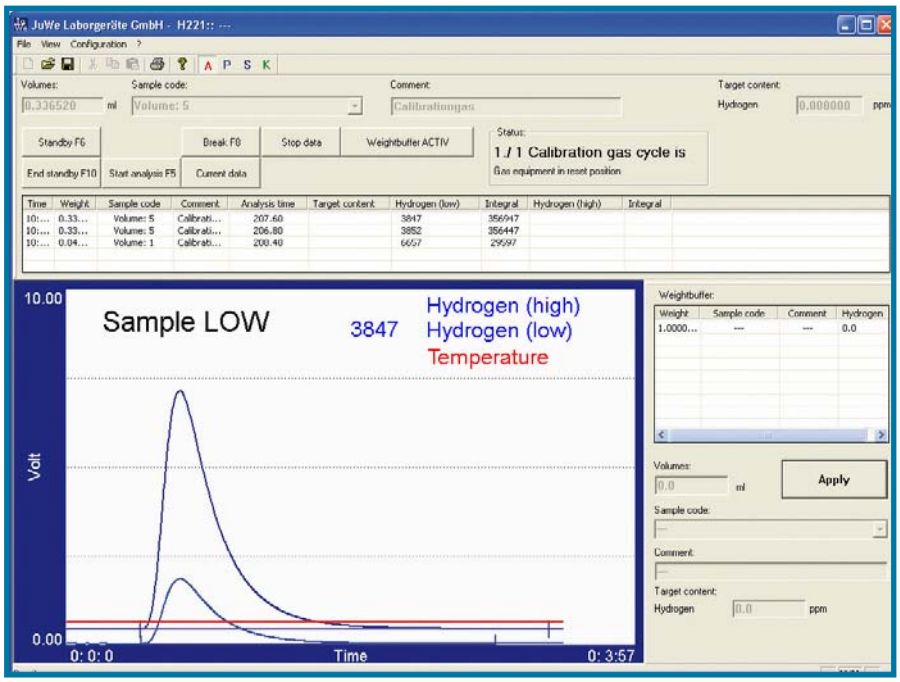


Fig. 3. *The analysis screen of the "G4 Phoenix DH".*

Measuring procedures

One of the reference procedures for the determination of hydrogen in welds is the so-called mercury method in which the hydrogen is extracted underneath mercury in a vacuum at room temperature.

Disadvantages of this procedure are not only the long measuring times of 72h or more but also the manual reading-off of

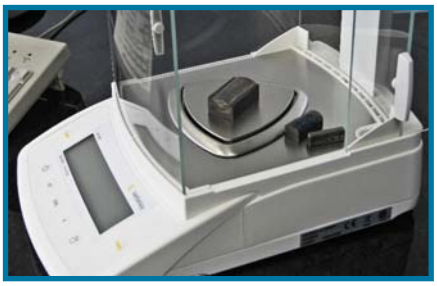


Fig. 4. *Weighing of the central part for the sample preparation.*

the results from a burette and the handling of the toxic heavy metal mercury.

Moreover, a global ban on the use of mercury has been decided within the framework of the UN Environmental Programme (UNEP) as from 2011.

A time-saving and easy-to-handle alternative is the so-called or hot extraction procedure in a tube furnace with the subsequent detection of the hydrogen using a thermal conductivity detector. In the case of this method, the sample which is located in a quartz tube is heated in an inert gas flow according to DINEN ISO 3690 and the hydrogen released from the material is transported through the thermal conductivity cell with the carrier gas flow. The time-related integral of the measured signal corresponds to the hydrogen content in the sample.

The higher temperature leads to a higher diffusion rate of the hydrogen in the material. Substantially shorter analysis times of 10 to15min in comparison are achieved in this way. In a national round robin test, the hot extraction procedure was rated as a reference procedure equivalent to the mercury method.

The functioning method

The "G4 Phoenix DH" analyser, Fig. 1, serves to determine the diffusible hydrogen in the most diverse matrices by means of hot extraction in a carrier gas flow. The analysis device has a quickly heating and cooling hinged infrared furnace and/or a wire-wound resistor furnace, both equipped with a quartz tube for heating up the sample material, Fig. 2.

The temperature-programmable infrared furnace is utilised for the investigation of the diffusible hydrogen content in welded samples. The tube diameter of the

Fig. 5. *After the pushing-in of the sample and the start of the measurement: automatic sequence of the analysis operation.*

infrared furnace is 30 mm. Thus, it is no problem to analyse even large samples according to DINENISO 3690 and AWS A4.3 at the planned extraction temperature of 400°C.

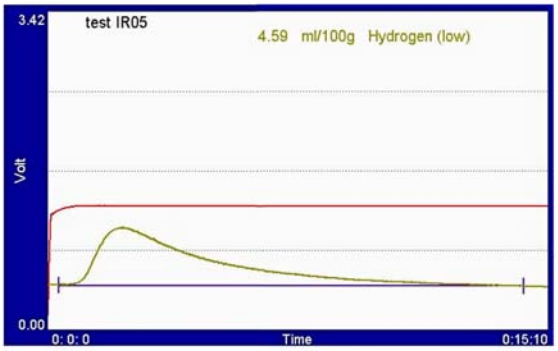
Pure nitrogen is used as carrier gas. The thermal conductivity detector which is highly sensitive and stable in the long run and with which even lowest hydrogen contents can be detected forms the heart of the analysis device. The automatic gas calibration unit with ten different volumes guarantees simple and reliable calibration.

The released diffusible hydrogen is transported through the thermostatised thermal conductivity detector with the carrier gas. The change in the thermal conductivity in comparison with the reference side is detected by thermistors in a bridge connection.

In the course of the measurement, the measured signals are displayed on line on the monitor. The area underneath the resulting measured signal is proportional to the hydrogen content of the sample. With the aid of the calibration factor or the calibration function, the hydrogen concentration of the sample is established from the time-related integral taking account of the sample weight.

The analysis software of the "G4 Phoenix DH" has a clear and simple structure. All the tasks are displayed in an intelligible form on four different screen pages:

- ☐ analysis screen, Fig. 3:
  execution of the analysis, graphic output of the signal course etc.,
- ☐ parameters screen:
  setting of the analysis parameters and saving of configurations for different analysis methods,
- ☐ statistics screen:
  statistical evaluation of the analyses as well as
- ☐ calibration screen:
  calibration of the device; single-point, two-point or multipoint calibration.



Sample code:	123456
Comment:	G1
Date:	29.08.2008
Weight:	6.327 g
Hydrogen (low)	
Result:	2.4362 ml/100g
Target content:	2.5000 ml/100g
Factor:	465
Blindvalue:	0
Investgating Laboratory:	Testcompany
Investigator's name:	John Smith
Electrode material:	Electrode material
Batch No.:	2
Type of electrode:	Type of electrode
Electrode Designation:	Electrode Designation
Diameter of electrode (mm):	1.2 mm
Overall length (mm):	100 mm
Electrode polarity:	d.c. +ve
Cone angle:	30°
Rel. humidity during welding (%)	30
Temp. during welding (%):	25°C
Hydrogen extraction temp.(°C):	400°C

Fig. 6. *Report and graphic display of an analysis.*

Sample	Hydrogen [ml/100g]	Average	Standard deviation
X5S1_1	1,025		
X5S1_2	1,086	1,0573	0,0307
X5S1_3	1,061		
X5S3_1	2,4932		
X5S3_2	2,4941	2,4947	0,0019
X5S3_3	2,4968		
X5S5_1	4,356		
X5S5_2	4,324	4,3393	0,0160
X5S5_3	4,338		

Sample	Variation coefficient	Minimum	Maximum
X5S1_1			
X5S1_2	0,02900	1,025	1,086
X5S1_3			
X5S3_1			
X5S3_2	0,00075	2,4932	2,4968
X5S3_3			
X5S5_1			
X5S5_2	0,00370	4,324	4,356
X5S5 3			

Fig. 7. *Typical analysis results.*

Sample preparation

A water-cooled copper holder into which the substrate material for the weld is clamped is used for the production of the welded samples according to DINEN ISO 3690. The base material to which the weld is applied must be clean and grease-free and must be degassed for approx. 1h at 650°C beforehand. It consists of three sections, the central part as the test piece and the min. 50mm long run-in and run-out pieces. The central piece is weighed, Fig. 4, and is provided with a code for identification purposes.

Directly after the end of the welding process, the test piece is taken out of the holder, is quenched in iced water for approx. 5s and is immediately transferred into a cooling vessel with methanol / dry ice or liquid nitrogen. Both work steps, the welding and the cooling of the sample, should be taken in one step and in controlled conditions. After approx. 2min cooling, the run-in and run-out parts can be separated from the central test piece.

Until the analysis, the test pieces with the weld to be investigated can be stored at -78°C for around 72h and, in the liquid nitrogen, at -196°C for approx. 21 days. For the analysis, the sample is taken out of the cold bath, warmed up in water, rinsed with acetone and dried with cold air. Immediately thereafter, the test piece is weighed and the mass of the weld is calculated from the difference to the dead weight established before the welding.

The "G4 Phoenix DH" permits the automatic determination of the sample weight by previously saving the dead weights of the corresponding test pieces. Immediately after the weight has been input, the analysis is started and the sample is pushed into the quartz extraction tube.

Analyses

With the infrared furnace, the diffusible hydrogen contents of all the customary welded samples can be investigated thanks to the large quartz tube diameter of 30 mm, Fig. 5. After the start of the measurement and the pushing-in of the sample, the analysis proceeds automatically.

The report is drawn up and output according to the stipulations in DIN ENISO 3690, Figs. 6 and 7.

Conclusion

With the hot extraction method, an innovative, internationally acknowledged and precise measuring procedure which offers substantial time savings compared with the mercury method is available for the determination of the diffusible hydrogen. Moreover, it is not necessary to handle the toxic mercury.

The "G4 Phoenix DH" analyser offers not only uncomplicated handling and the easy-to-operate software but also an automatic analysis sequence with results output in ppm or ml/100 g. The programmable, quickly heating infrared furnace permits a large number of applications.

The taking of the measurements with the "G4 Phoenix DH" as well as the analysis report structure conform not only with the AWS A4.3 standard but also with DINEN ISO 3690.

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Literature

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