Dedicated Hydrogen Solutions in Steel and Welding

Audience Poll

Did you know that diffusible hydrogen is very important to measure in the steel and welding industry?

- Yes
- No
- Somewhat

Content
Dedicated Hydrogen Solutions

- Introduction to our speakers
- What is hydrogen
- Why does hydrogen need to be analyzed
- Instrument configuration
- Hydrogen in steel
- Hydrogen in automotive
- Hydrogen in welding
- Q & A Session

Welcome!
Meet your speakers

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What is Hydrogen?

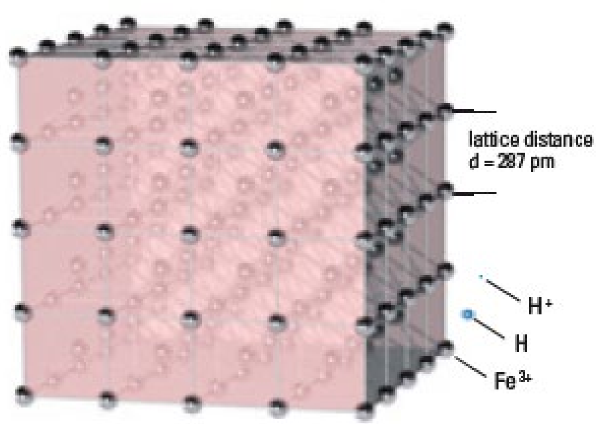
Hydrogen Theory

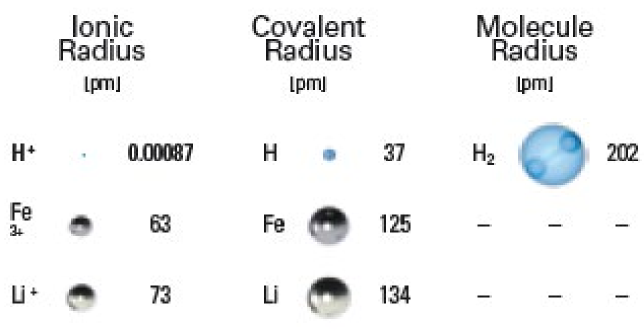
What is Hydrogen?

Hydrogen is:

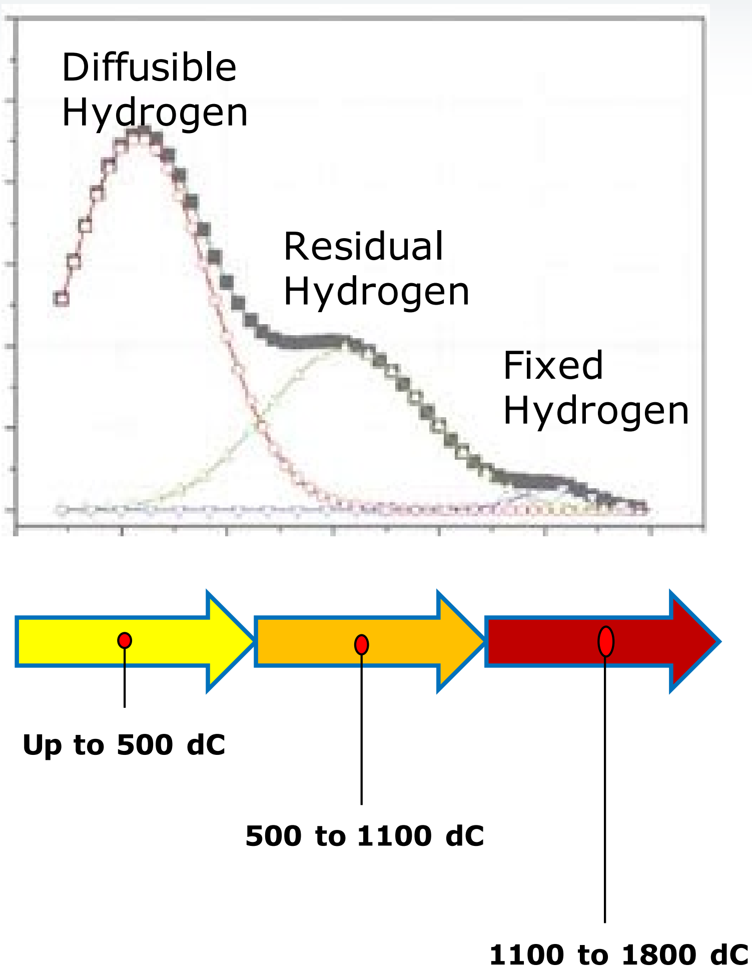
- Most common element in nature
- Lightest element in the periodic table
- Element with the smallest atomic diameter
- Element with the highest diffusion rate through a metal lattice
- Element with the highest impact to form cracks in high strength steel, weldings and oxygenated copper

Metal Lattice





Hydrogen Theory
Hydrogen Forms



Hydrogen in metals can be present as:

- Diffusible Hydrogen
  Hydrogen atoms, located on inter-stitials, high mobility, solubility increases with temperature
- Residual Hydrogen
  Weakly and strongly trapped hydro-gen molecules, not mobile, solubility decreases with temperature, splits into atoms with thermal activation
- Fixed Hydrogen
  Stable hydrides, bound to the metal e.g. V, Mg, Li, La, Ti, …

Why do we need to measure hydrogen?

Hydrogen Theory

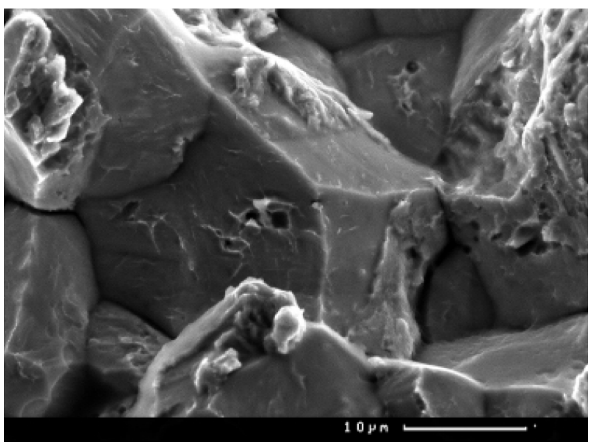
Why Hydrogen Analysis?

- Steel Plants produce new steel grades for high end industries with increased cracking behavior because of hydrogen
- Automotive Industry uses new manufacturing techniques which are also related to hydrogen cracking
- Welding Industry works with an high influence of hydrogen into the welding
- Aluminum has a high affinity to pick up hydrogen, which reduces the quality
- Titanium and other precious metals are moving forward in Aerospace and Medical Implants (especially related to 3D printing), which needs a control of total Hydrogen
- Hydrogen in copper reduces the mechanical properties and has an influence during the use in power industry (cables, wires,..)
- Hydrogen in ceramics or other powders indicates the moisture content

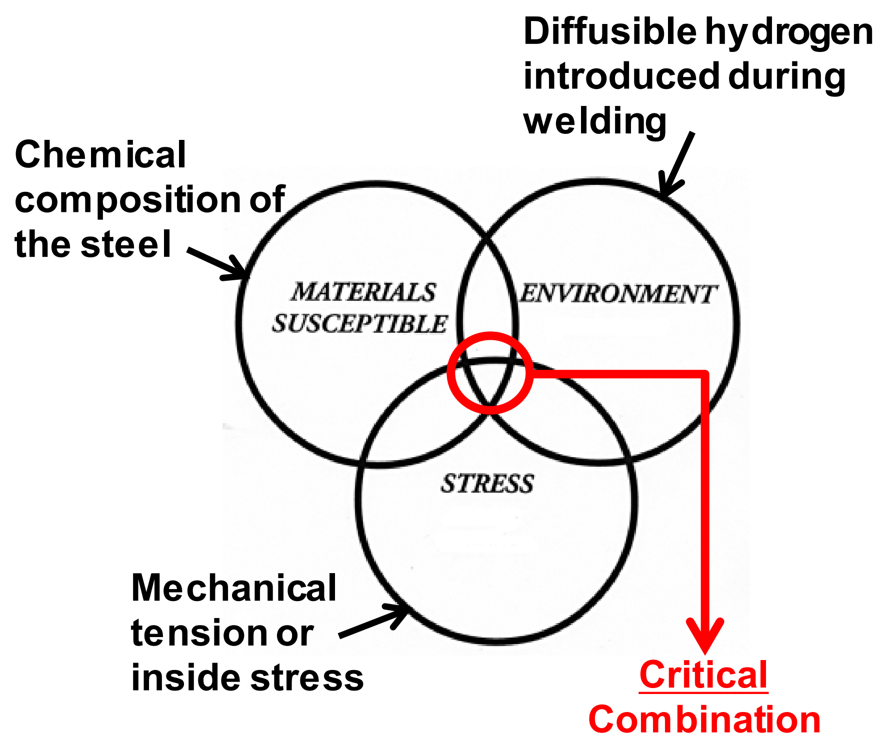
Hydrogen Theory
Hydrogen Embrittlement

Embrittlement is a phenomenon that causes loss of ductility in a material, thus making it brittle. There are several different forms including:

- **Environmentally Induced Cracking**
- **Stress Corrosion Cracking**
- **Hydrogen Embrittlement**
- **Corrosion Fatigue**
- **Liquid Metal Embrittlement**



Intergranular fracture surface of a hydrogen-induced brittle fracture



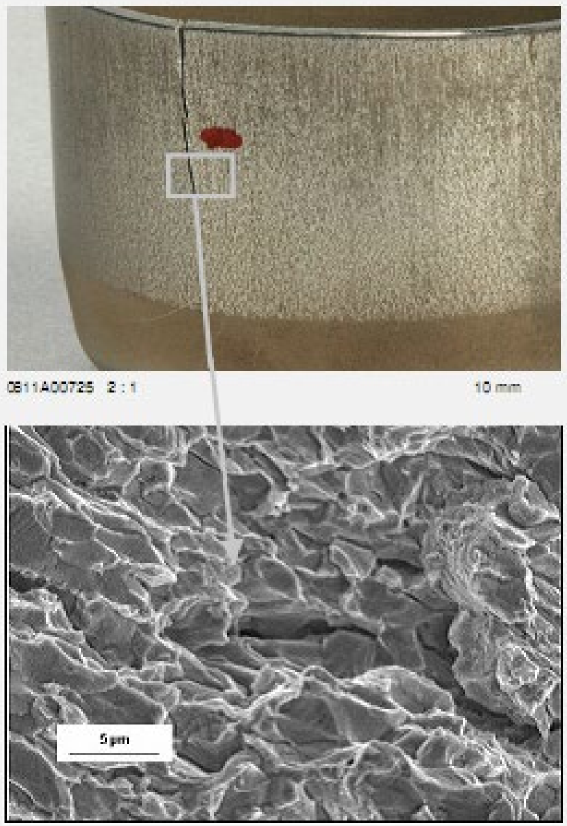
Hydrogen Theory
Hydrogen Embrittlement

Video removed for protection

Hydrogen Theory

Hydrogen Embrittlement – Crack Formation

Delayed cracking in high strength steels



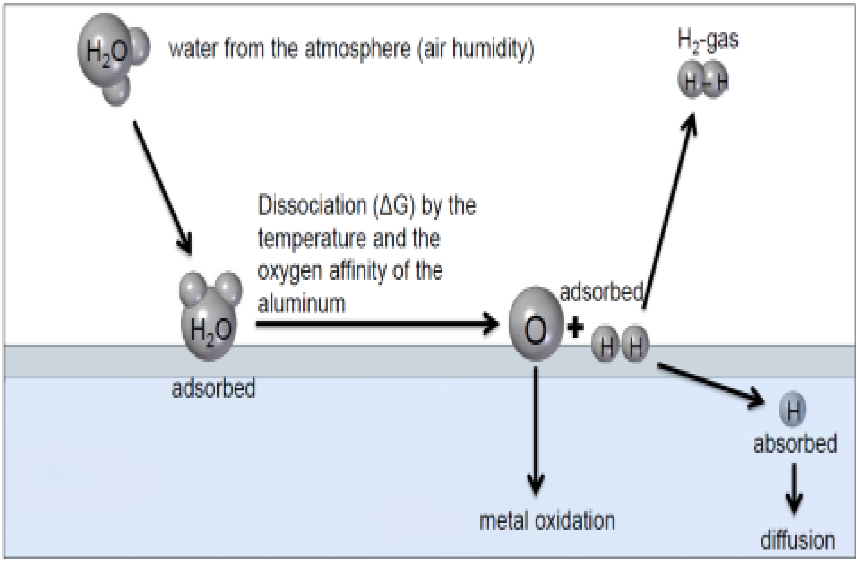
- Hydrogen induced delayed fracture
- Intercristalline fracture

ThyssenKrupp Steel Europe

ThyssenKrupp

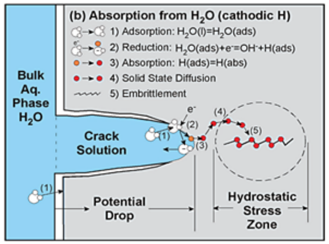
Sources of Hydrogen

- Hydrogen can penetrate metals during almost each manufacturing or processing step (e.g. melting, etching, annealing...) but also in component life (corrosion). Main H-source (and O-source): **Water !**

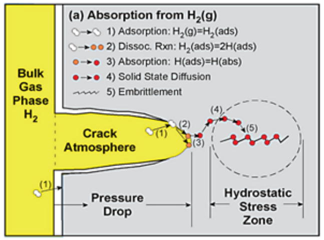


Hydrogen molecule is 26 x bigger in volume

- From the gas phase
  - Adsorption of moisture on metal surface, followed by dissociation
  - Catalytic effects on metal surface, heat, mech. stress etc. support the dissociation



- Form liquid phase (pickling, electroplating, …)
  - Acidic media: H^+ move to metal surface and further …
  - Dissociated H atom diffuses into lattice



Instrument Configurations

Instrument configurations

G4 PHOENIX vs. G6 LEONARDO vs. G8 GALILEO

Analysis of Total Hydrogen	X	✓	✓
Analysis of diffusible Hydrogen	✓	X	✓
Analysis of residual Hydrogen	✓	X	✓
Analysis of Hydrogen in Aluminum	X	X	✓
Gas Calibration Unit	✓	X	✓
Add On Oxygen Analysis	X	✓	✓
Add On Nitrogen Analysis	X	✓	✓
Add On Argon Analysis	X	X	✓
Add On Mass Spectrometer	✓	X	✓
Add On Degassing Unit "YANAKO"	✓	X	✓
Molecular Sieve Reagent Tubes	✓	X	✓

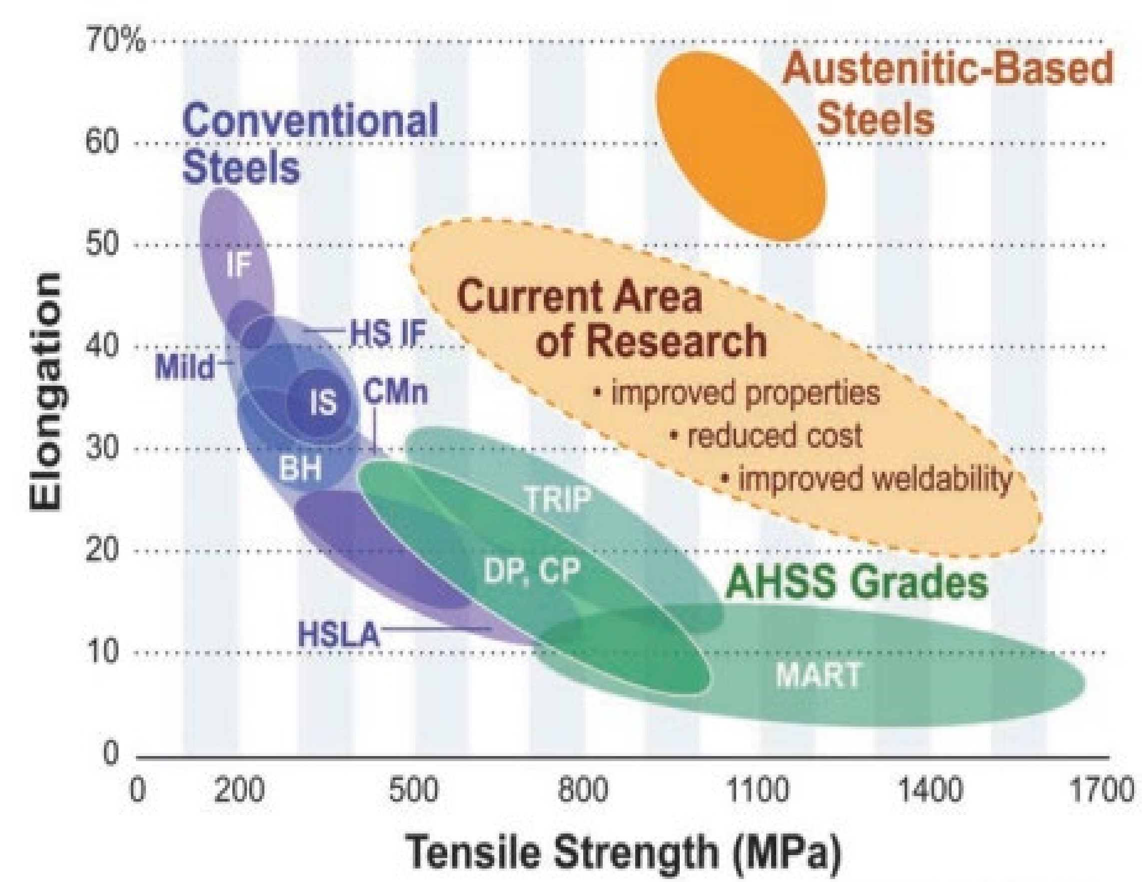
Bruker – Best Solutions

Hydrogen Analysis

- Total hydrogen analysis using a direct temperature controlled method (optical pyrometer)
- Most precise and stable Thermal Conductivity Detector with detection limits down to 0.01 PPM
- High precise 10 volume gas calibration unit
- Additional Mass Spectrometer for ultra-low hydrogen detection
- Diffusible, Residual, and Total hydrogen measurement all in one system
- Knowledgeable Sales, Service, and Application support

Hydrogen in Steel

Hydrogen in Steel
High Strength Steels

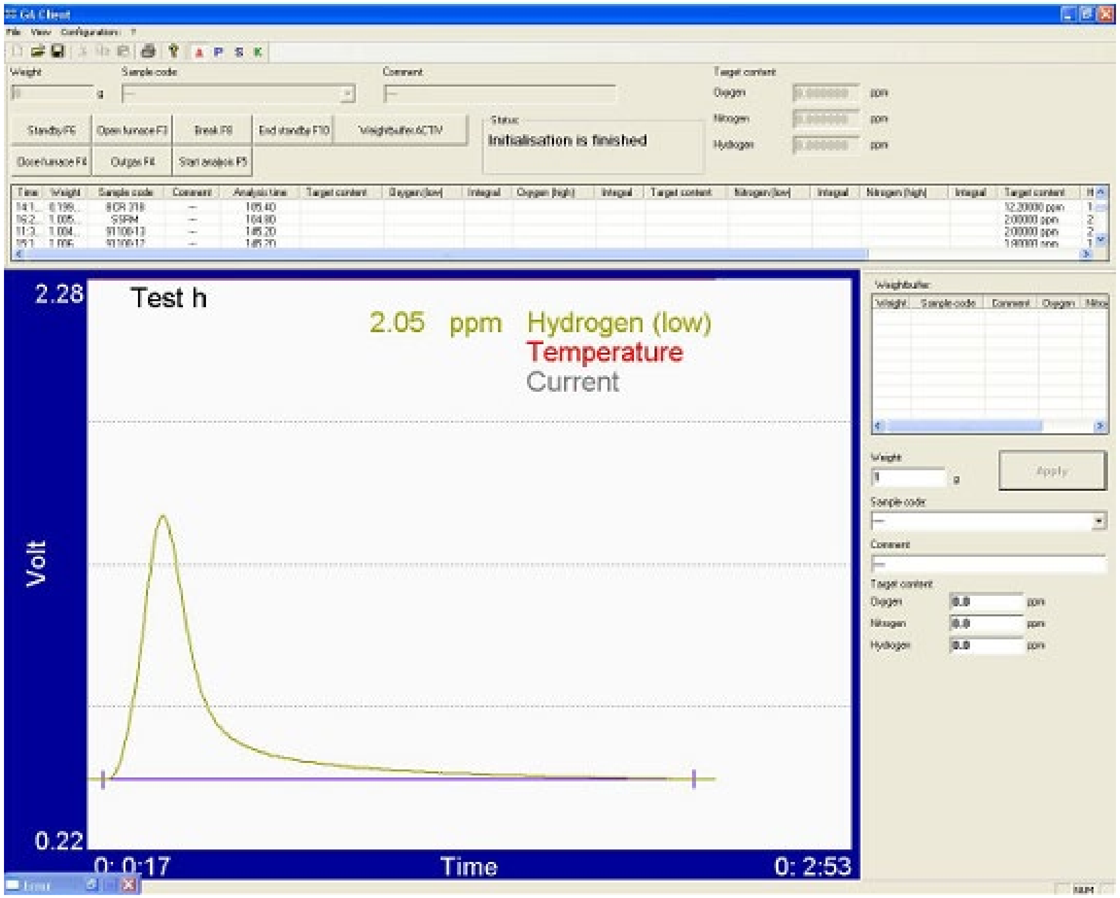


Tensile Strength above 800 MPa → High Strength

HSS and AHSS are current steel grades that provides :

- ✓ Higher strength
- ✓ Improved ductility
- ✓ Improved mechanical properties, like high strain-hardening capacity
- ✓ Improved weldability
- ✓ Improved formability
- ✓ Selected chemical composition
- ✓ Multiphase microstructures

Hydrogen in Steel
Total Hydrogen Analysis



IGF = Melt Extraction
@ 1,500 dC

Typical results steel sample

Weight/g	Time/s	H/ppm
1,0053	105	2.05
1,0038	104	1.97
1,0077	105	1.93
1,0045	104	2.02
1,0022	105	2.03

Average: 2.03

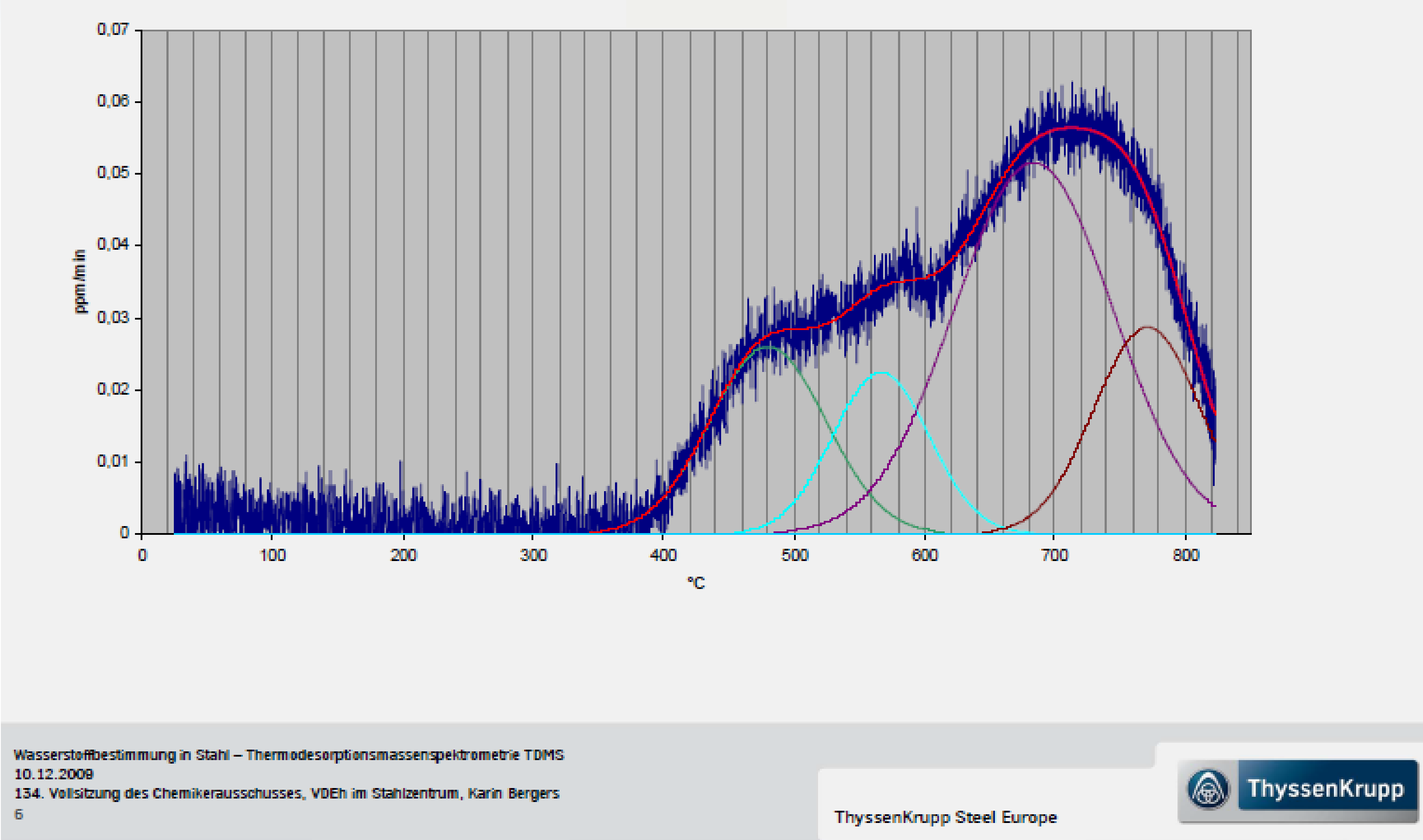
Std. deviation: $\pm$ 0.09

Hydrogen in Steel

TDS and/or TDMS Method

- It is known that hydrogen in steel is prone to be trapped at various structural defects or particles such as grain boundaries, dislocations, carbide and inclusion interfaces, microvoids, point defects and so on.
- TDS = Thermal Desorption Spectroscopy or TDMS = Thermal Desorption Mass Spectroscopy are used to analyze the hydrogen diffusion coefficient. Based on experimental data using Carrier Gas Hot Extraction Method, a numerical model has been developed to describe the hydrogen transport and respective hydrogen distribution at elevated temperatures.
- TDS has been often used to analyze the trapped state of hydrogen. The hydrogen trapping sites can be identified by calculating the activation energy of hydrogen desorption
- When two types of trap are present, the release of hydrogen from the respective trap will appear at two temperatures. By changing the heating rates (0.1, 0.33, 0.75, 1.0 K/s), different peak temperatures could be obtained for a kind of trap in the hydrogen desorption curve
- The low-and high-temperature hydrogen desorption peaks were then calculated in kJ/mol, respectively.

Hydrogen in Steel
TDS and/or TDMS Method

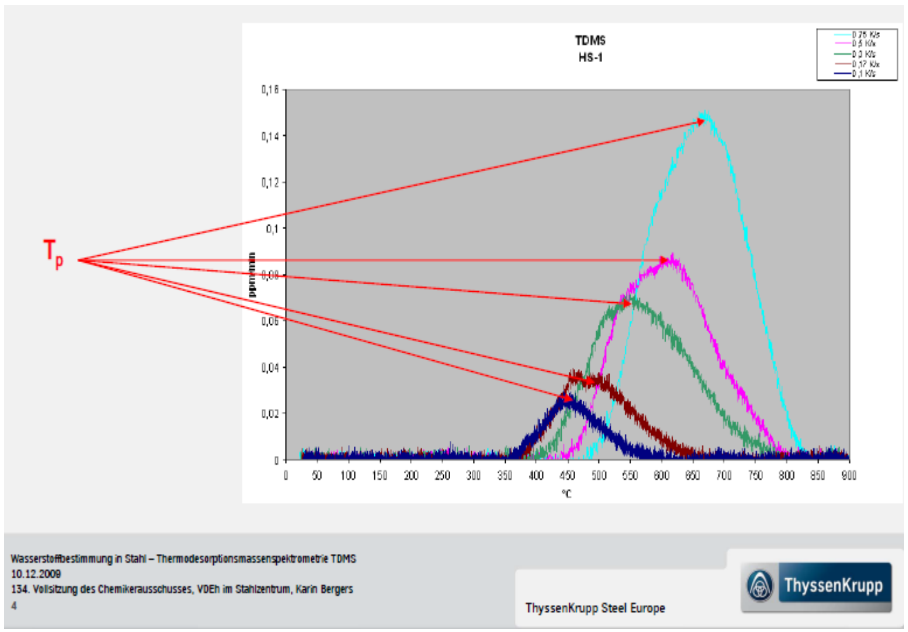


Example of different peaks (Hydrogen Traps) after external peak deconvolution

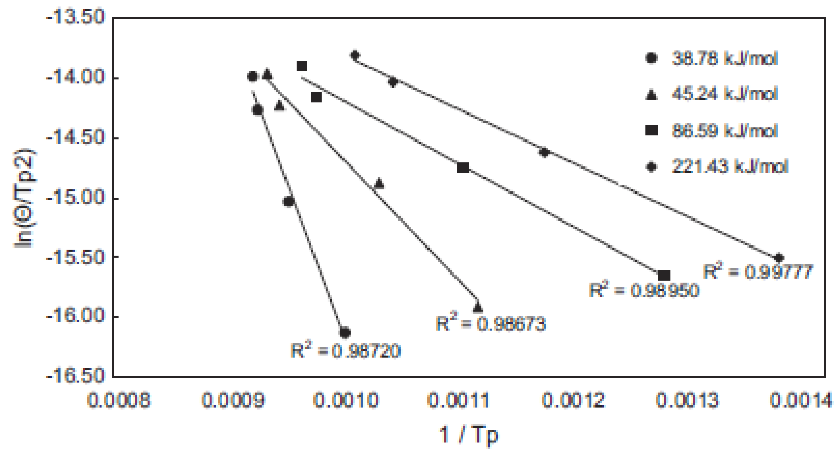
Hydrogen in Steel

TDS and/or TDMS Method

Determination of Hydrogen in Steel by Thermal Desorption Mass Spectrometry;
Steel Research Int. 81 (2010) No. 7;
K. Bergers, E. Camisao de Souza, I. Thomas, N. Mabho, J. Flock



Example of different heating rates



	0.1 K/s	0.33 K/s	0.75 K/s	1 K/s
Trap 1	9.38%	22.53%	52.69%	38.51%
Trap 2	7.69%	5.24%	21.51%	25.85%
Trap 3	70.97%	46.47%	19.31%	19.62%
Trap 4	11.96%	41.12%	11.03%	8.69%

Hydrogen in Automotive

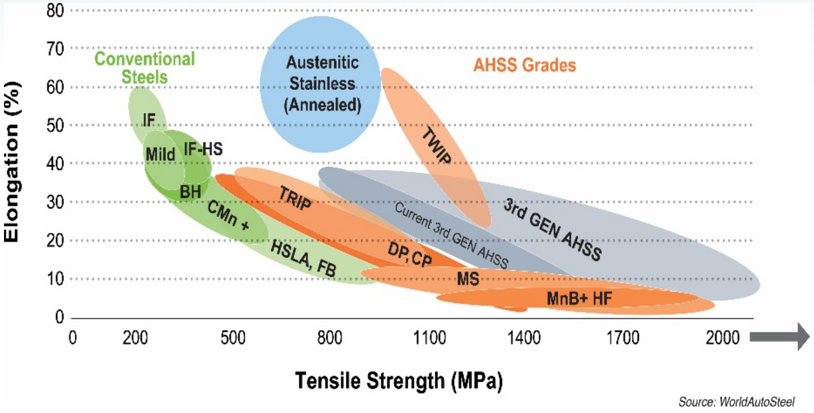
Hydrogen in Automotive

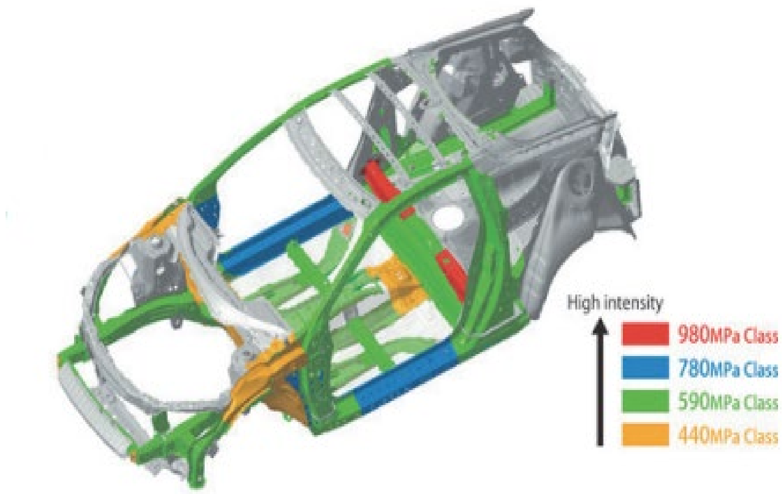
Why needed?

- In order to reduce CO_2 emissions, fuel consumption, and to respect current environmental norms, the reduction of a vehicles weight is a primary target of the automotive industry. Advanced High Strength Steels (AHSS) and Ultra High Strength Steel (UHSS), which present excellent mechanical properties, are increasingly used in vehicle manufacturing. The increased strength to mass ratio compensates the higher cost per kg, and AHSS and UHSS are proving to be cost-effective solutions for car manufacturers.

- In particular, aluminized boron steel can be formed in complex shapes with press hardening processes, acquiring high strength without distortion, and increasing protection from crashes. On the other hand, its characteristic martensitic microstructure is sensitive to hydrogen delayed fracture phenomena and, at the same time, the dew point in the furnace can produce hydrogen consequently to the high temperature reaction between water and aluminum. The high temperature also promotes hydrogen diffusion through the metal lattice under the aluminum-silicon coating, thus increasing the diffusible hydrogen content. However, after cooling, the coating acts as a strong barrier preventing the hydrogen from going out of the microstructure. This also increases the probability of delayed fracture. As this failure brings to the rejection of the component during production, or, even worse, to the failure in its operation, diffusible hydrogen absorbed in the component needs to be monitored during the production process.

Hydrogen in Automotive
TDA Analysis





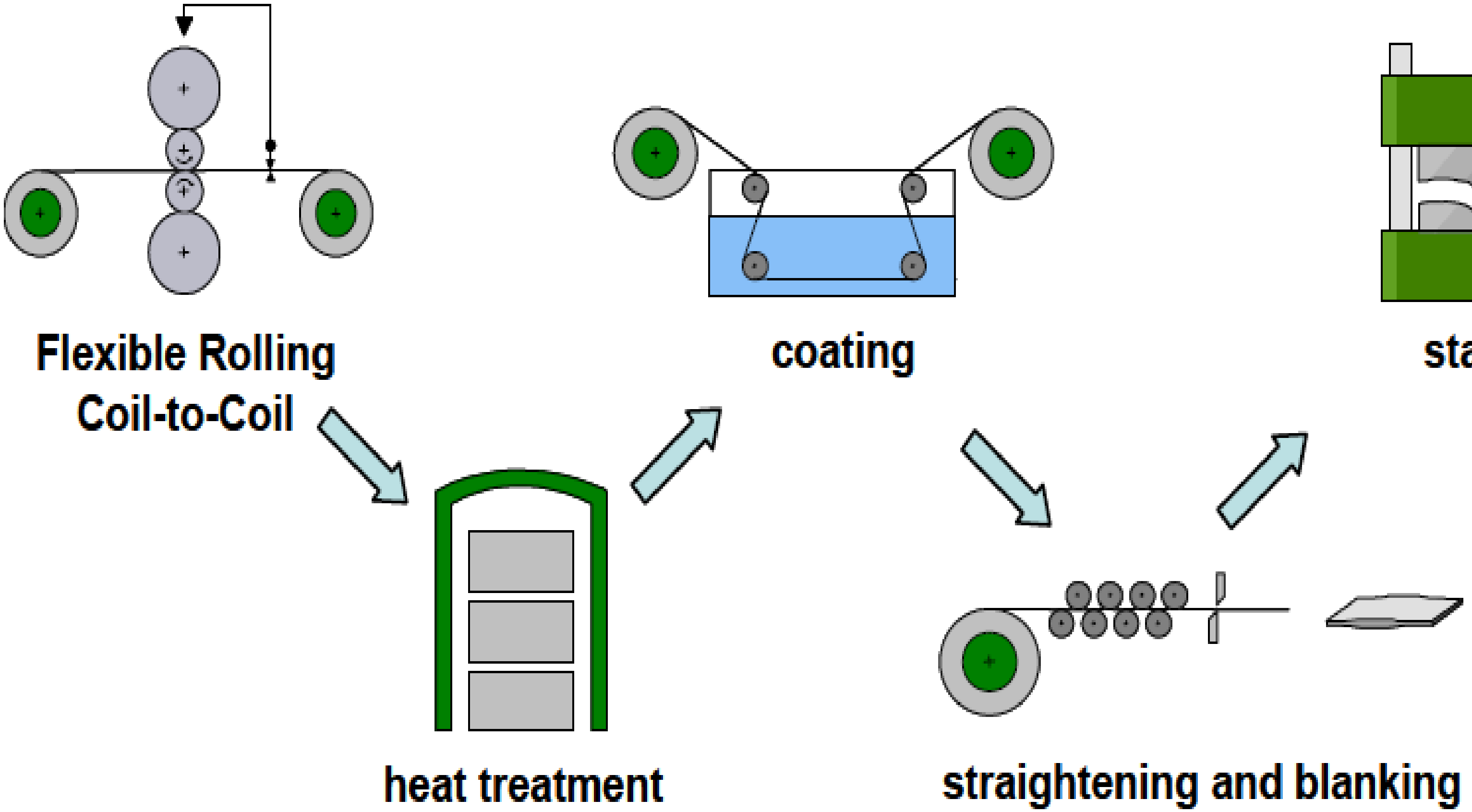
Parts of HSS @ Honda

<u>Advantages</u>

- Lightweight potential > 20% per component
- Weight reduction up to 15 kg per vehicle
- Competitive lightweight design costs
- High material utilization (> 60%)
- High degree of design freedom with sheet thickness variations
- Number of sheet thickness variations does not affect cost

Hydrogen in Automotive

"Tailor" Products



Typical results of diffusible Hydrogen after heat treatment between 0.6 – 0.8 ppm

Hydrogen in Automotive

Round Robin TDA Analysis

VOLKSWAGEN
AKTIENGESELLSCHAFT

Results

VW – Volkswagen AG
MPA – Max-Planck-Institute
IWF – Institute of Material Science
VA – Voestalpine,
TKS – Thyssen Krupp Steel,
BAM – Federal Bureau for Reference Materials

#	Labor	Probe 1 [ppm]	Probe 2 [ppm]	Probe 3 [ppm]	Probe 4 [ppm]	Probe 5 [ppm]	Probe 6 [ppm]	MW	Stabw.
1	**VW**	0,26	0,25	0,25	0,22	0,21	0,25	***0,24***	*0,02*
2	**IWF**	0,28	0,23	0,28	0,22	0,24	0,20	***0,24***	*0,03*
3	**TKS**	0,24	0,21	0,23	0,23	0,21	0,21	***0,22***	*0,01*
5	**MPA**	0,26	0,28	0,23	0,21	0,27	0,30	***0,26***	*0,03*
6	**VA**	0,20	0,31	0,25	0,42	0,15	0,23	***0,26***	*0,09*
3	**BAM**	0,24	0,25	0,25	0,25	0,22	0,24	***0,24***	*0,02*
	MW	**0,25**	**0,26**	**0,25**	**0,26**	**0,22**	**0,24**		
	Stabw.	*0,03*	*0,04*	*0,02*	*0,08*	*0,04*	*0,04*		

Round Robin Test organized by Bruker of Steel Plates supplied by Volkswagen

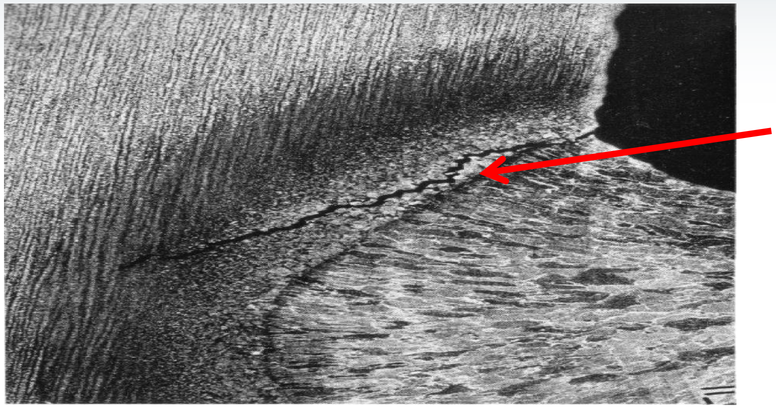
Hydrogen in Welding

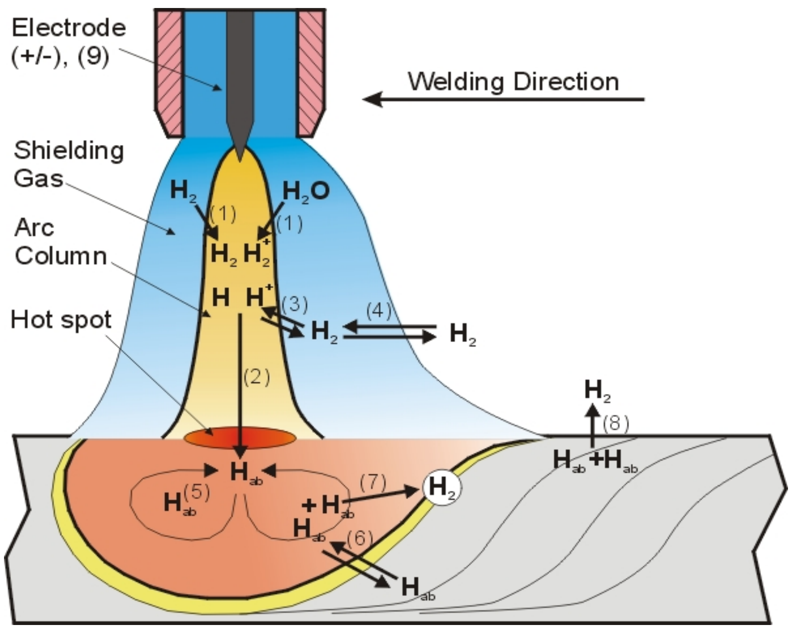
Hydrogen in Welding
Why is it needed?

- In welding, hydrogen is generated from the dissociation of water vapor or hydrocarbons in the welding arc
- Metals such as steel and aluminum at or near their melting temperatures diffuse hydrogen at a very high rate
- Therefore, the molten weld metal can rapidly pick up hydrogen from the hot gas in the arc
- Once in the weld metal, hydrogen atoms can diffuse easily into the heat-affected zone (HAZ) of the base metal, as diffusible hydrogen ([H]D), because their diameter is much smaller than the lattice size of the metals
- The driving force to form diatomic or molecular hydrogen inside the weld is so great that pressure may increase. This induces localized tensile stresses that add to residual tensile stresses, which finally ends up in hydrogen induced cracks, named hydrogen embrittlement

Hydrogen in Welding

Sources of Hydrogen in Welding





Cold cracks in welded joints can be caused by hydrogen which enters the material during the fusion welding process.

The hydrogen in H-induced cold cracks originates primarily from humidity

- from the welding filler material
- from the ambient atmosphere
- from additives
- from condensed water near the joining zone

Hydrogen in Welding

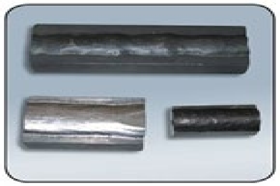
Classification of Welding Consumables

SZ	Coated Stick Electrode				Welding Powder	
Norm	DIN EN ISO 2560: 2010-03		AWS SFA-5.1/SFA-5.1M:		DIN EN ISO 14171: 2016-12	
	HD-Content [ml/100g SG]	Marked as	HD-Content [ml/100g SG]	Marked as	HD-Content [ml/100g SG]	Marked as
ultra low					2	H2
			4	H4	4	H4
	5	H5			5	H5
low			8	H8		
	10	H10			10	H10
high	15	H15			15	H15
			16	H16		

Different hydrogen classifications in welding consumables according to different norms

Hydrogen in Welding
Norms & Methods

Welding Norms:

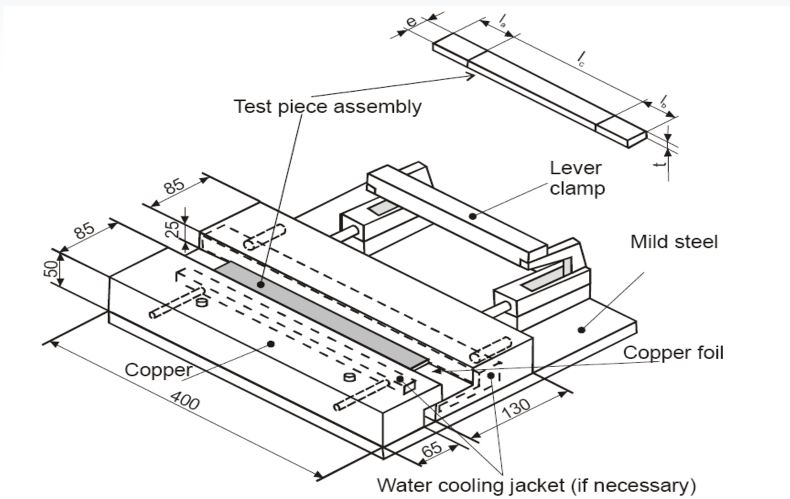


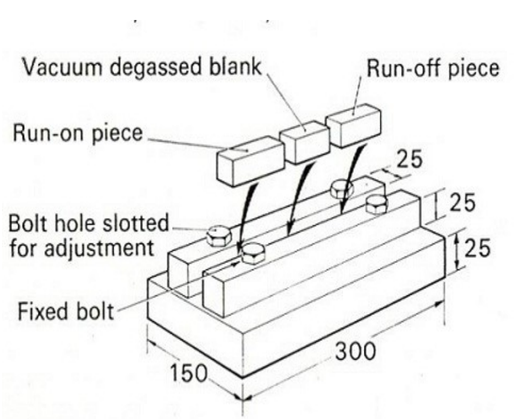
- ISO 3690 (Europe)
- JIS Z 3118 (Japan)
- AWS 4.3 (USA)
- other local norms

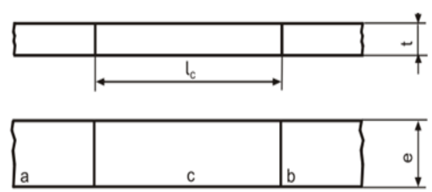
Different Methods	**Advantages or Disadvantages**
Mercury Method	toxic liquid mercury, 72 h, up to 50 ° C
Glycerin Method	low accuracy, still too long (72 h)
Hot Extraction Method	high accuracy and shorter
✓ Direct method with TCD detection **(G4 PHOENIX)**	most precise and reliable, fastest (20-60 min per sample), up to 900° C
✓ Indirect method with Gas Chromatography with gas collection	precise, but still too long minimum 6-24 h for 4 samples, up to 150° C

Hydrogen in Welding

Sampling & Sample Preparation







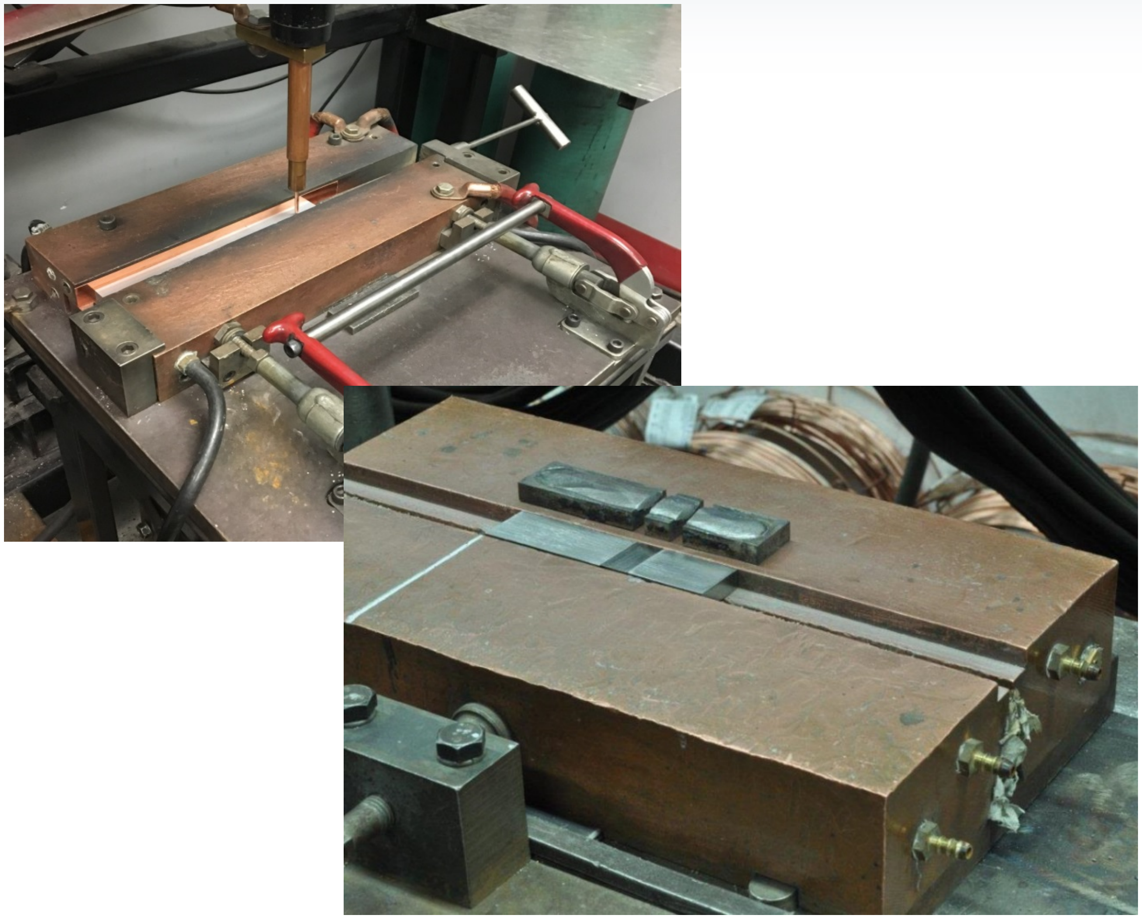
Dimensions in millimetres

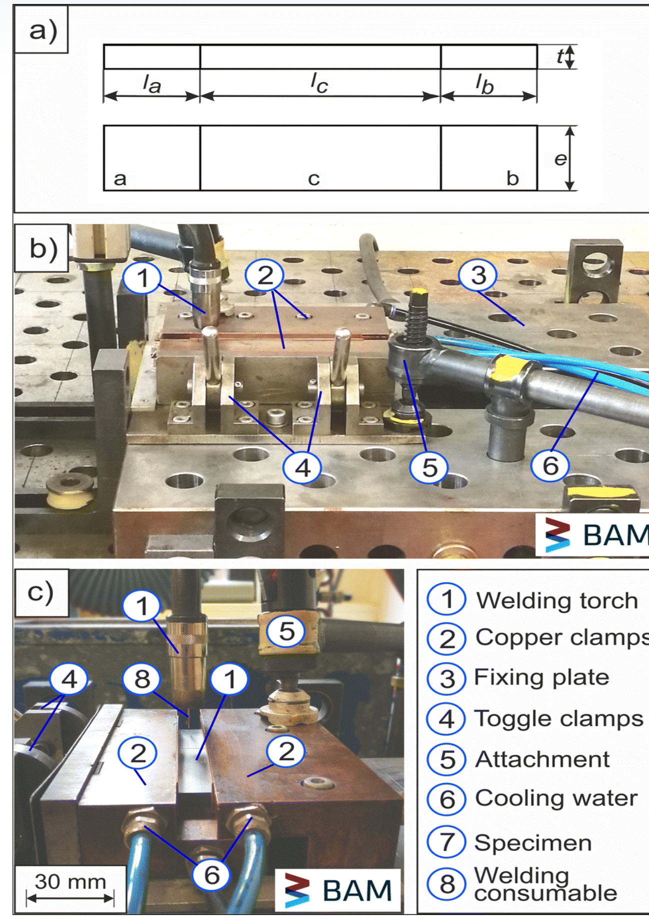
Test assembly		$l_a = l_b$	l_c	e	t
A [a]		Min. 25 (50)	80	25	12
B		Min 25 (50)	30	15	10
C		Min 50	15	30	10
a/b	Run-on / Run-off test piece.				
c	Centre test piece.				
$l_a = l_b$ = >25 mm: MMAW $l_a = l_b$ = >50 mm: other welding processes					
[a] comparable to the specimen geometry according to AWS A4.3-93 [5]					

- Steel: sampling from the melt with a vacuum tube, quick quenching in water, storage in liquid nitrogen or dry ice
- Weldseams: preparation of specimen acc. to ISO 3690, quick quenching in water, storage in liquid nitrogen or dry ice
- For analysis: take out the sample from the repository, warm-up with water, rinse with acetone, dry with a cold air blower, analyse immediately

Hydrogen in Welding

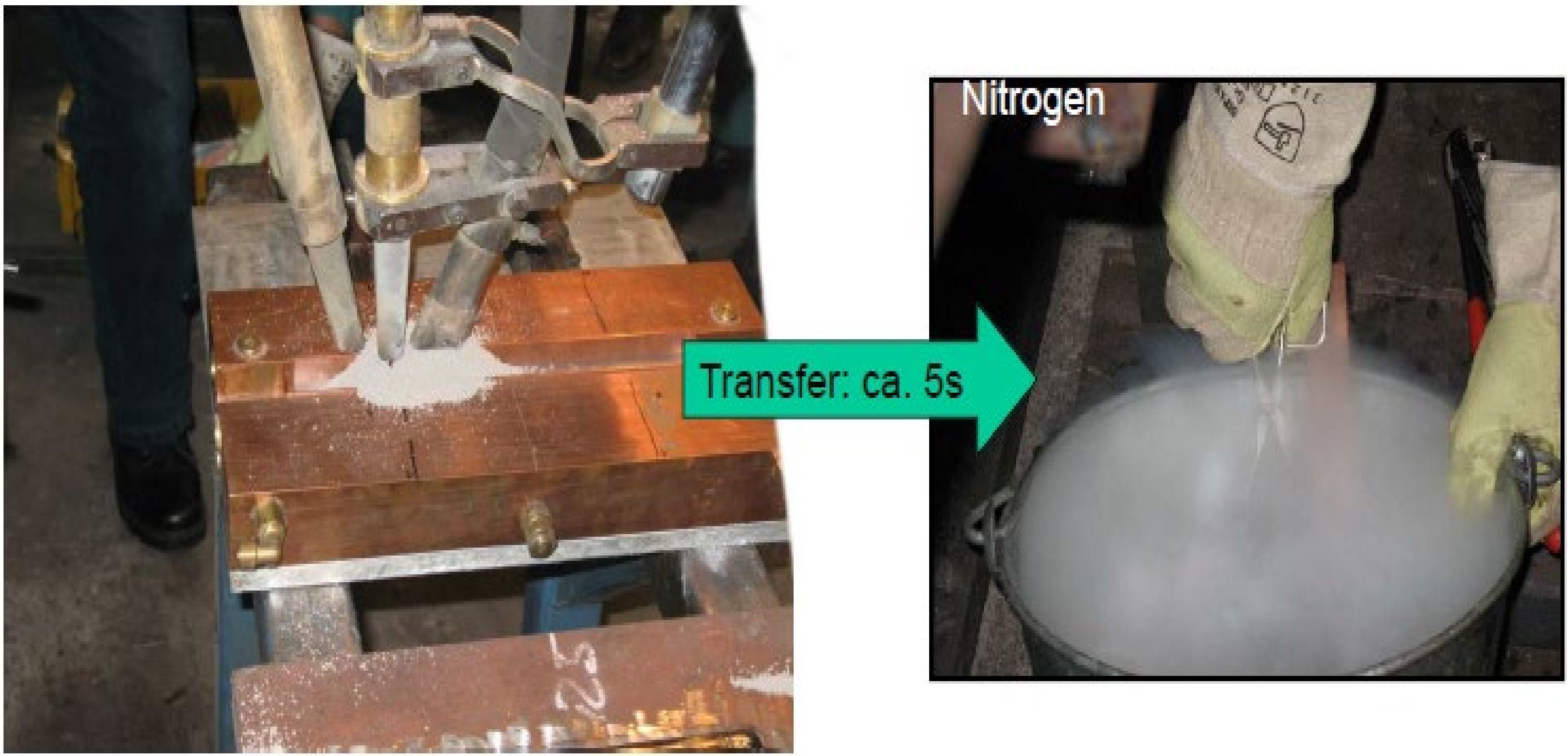
Sampling & Sample Preparation





Welding Process according to ISO 3690 or AWS 4.3

Hydrogen in Welding
Sampling & Sample Preparation



Welding Process according to ISO 3690 or AWS 4.3

Hydrogen in Welding
Bruker Hot Extraction Method

AWS A4.3:1993-ADD1

Addendum 1

Standard Hot Carrier Gas Extraction Method

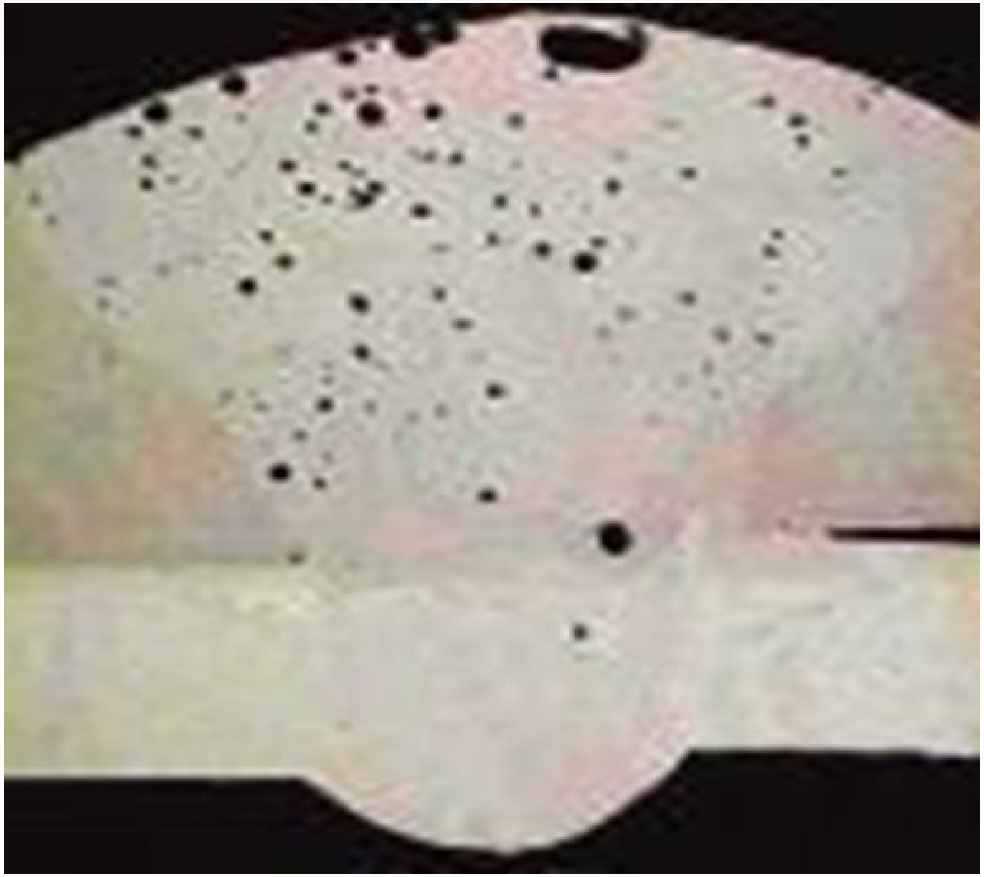
This addendum adds a third standard method of analysis to AWS A4.3:1993 and should be used in the same context as the two other standard methods of analysis prescribed in Clauses 7 and 8.

Hydrogen in Welding

Bruker Welding Analysis

		Hydrogen [ml/100g]	Average	Std. deviation
Sample 1	Welding 1	1.025		
	Welding 2	1.086		
	Welding 3	1.061	1.057	± 0.031
Sample 2	Welding 1	2.493		
	Welding 2	2.494		
	Welding 3	2.497	2.495	± 0.002
Sample 3	Welding 1	4.356		
	Welding 2	4.324		
	Welding 3	4.338	4.339	± 0.016

Hydrogen in Welding
Hydrogen in Aluminum Welds



Pores during Aluminum-Welding

- pores are metallurgically created gas inclusion
- they appear because of the high cooling speed of the mold
- the gas bubbles are trapped inside the metal structure
- mainly inside the weld, where they cause problems

Hydrogen in Welding

Hydrogen in Al-Welding-Wires

Weight (g)	Sample-ID	H (ml/100g)
0,2595	AlMg5-u	1,394
0,2646	AlMg5-u	2,247
0,2544	AlMg5-u	1,488
		1,71 ± 0,47
0,2726	AlMg5-g	1,133
0,2636	AlMg5-g	1,371
0,2658	AlMg5-g	1,203
		1,24 ± 0,12
0,2609	AlSi12-u	3,069
0,2612	AlSi12-u	3,085
0,2641	AlSi12-u	3,060
		3,07 ± 0,01
0,2569	AlSi12-g	0,971
0,2517	AlSi12-g	1,527
0,2555	AlSi12-g	1,223
		1,24 ± 0,28

Typical results by melt extraction (IGF)

SPECIAL THANKS

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Q & A Session

Innovation with Integrity