Special steel solutions
for hydrogen technology

Swiss Steel Group

With hydrogen towards CO_2 neutrality

Burning fossil materials to generate energy is causing significant damage to the global climate. On the other hand, the demand for energy is also growing worldwide and cannot nearly be covered by directly usable renewable energies such as wind and sun.

Hydrogen is the element that plays an important role in the transformation process towards climate neutrality.

Deutsche Edelstahlwerke and Ugitech, as steel producers of Swiss Steel Group, are committed to climate protection.

In addition to their own future use of hydrogen as a process gas, the steels produced by Deutsche Edelstahlwerke and Ugitech will support this demanding transformation process.

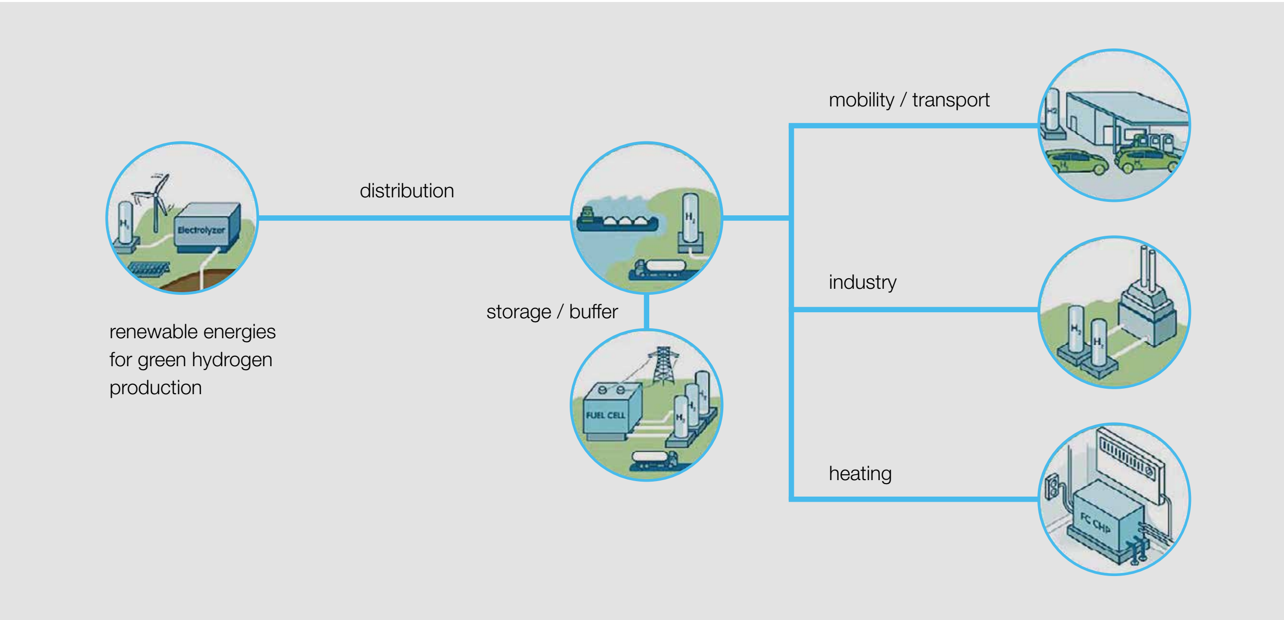

Fig. 1: Production, distribution and use of sustainable hydrogen

Unlike other renewable energies, hydrogen must be extracted from natural resources.
Probably the best known and most commonly used method for the production of sustainable H_2 is electrolysis, performed in large electrolyzers. The energy required for this shall be supplied by “green” electricity sources as wind or solar energy.

Once the hydrogen is produced, it is transported to its destination, either in gas or liquid phase, using either large tanks or appropriately designed pipelines.
At its final destination, the hydrogen has to be stored before it can be used.

The use of hydrogen will be manifold:
- Within mobility, hydrogen will be found in fuel cell technology or in combustion engines. Both technologies require tanks for the hydrogen supply.
- Hydrogen as a process gas requires different prerequisites compared to those for mobility. Due to the significantly higher quantities of hydrogen in the process, pipeline networks are more likely to be used here. However, as a process gas it will be directly used – without any conversion into electricity.
- Huge quantities of hydrogen will be needed for heating buildings as a substitute for oil or gas.
- Other application are seen as a basis for chemical reaction, e.g. using H_2 in combination with captured carbon for fertilizers.

Production, storage and use of H_2

Fig. 2: The production of sustainable H_2 requires energy generated by other renewable energy supplier as wind or photovoltaic systems. H_2 will be produced in an electrolyzer and finally either stored in various storage systems like tanks or directly transferred to pipeline networks.

Fig. 3: Hydrogen supplying stations for mobility

When the hydrogen is used in Fuel Cell Electric Vehicles (FCEV) or in Hydrogen Internal Combustion Engine Vehicle (HICEV), it must first be stored in hydrogen filling stations. The requirements for these tanks then again differ from the requirements for hydrogen vehicle tanks in mobility. The use of fuel cells or HICE is foreseen in various modes of transport, such as locomotives, trucks, ships and passenger cars.

Hydrogen is also suitable as an energy storage medium and can then be reconverted into electricity. However, these transformations are associated with high energy losses, which has so far prevented their economical use.

Demand for special steels

It is well known that hydrogen deteriorates the toughness properties of steel, caused by so-called hydrogen embrittlement.

As a rule, the tendency to embrittlement is significantly lower on austenitic steels. Austenitic stainless steels are commonly used for tanks, pressure cylinders and fittings. However, they are often designed for other than hydrogen applications.
Production, transport and storage of hydrogen require high pressures, which facilitate the diffusion of hydrogen and thus increase the threat of embrittlement.

Fig. 4 shows the influence of hydrogen on the mechanical properties for an engineering steel:

In a pressurized hydrogen atmosphere, the toughness properties such as elongation at fracture and reduction of area (RA) are significantly reduced. The yield strength and tensile strength are only slightly affected by hydrogen. The lower the strain rate in the test, the stronger the effect of hydrogen on the mechanical properties. This test under pressurized hydrogen is therefore carried out at the lowest possible strain rates.

A compromise has to be found between high mechanical properties and good resistance to hydrogen embrittlement:
new steel grades have to be developed and already established steels have to be tested for their suitability in hydrogen environments.

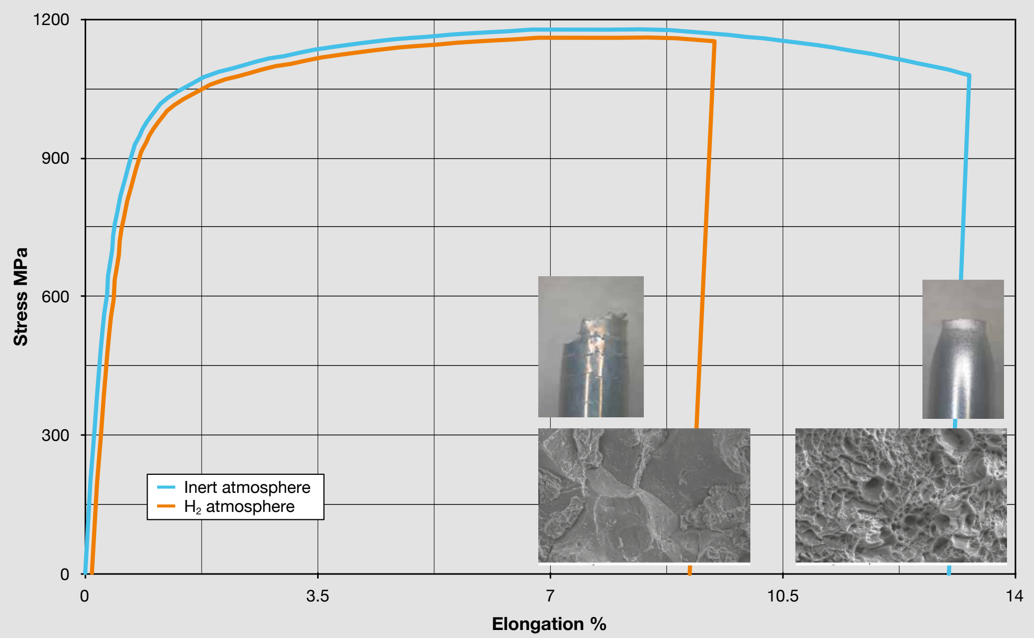

Fig. 4 Influence of hydrogen on the mechanical properties

In order to characterize the susceptibility to hydrogen embrittlement of the materials, the ratio RRA (Relative Reduction of Area) can be used as a criterion:
RRA describes the ratio between the reduction of area (RA) at the end of a tensile test obtained in hydrogen environment to that in inert gas (or any other hydrogen-free reference atmosphere): $RRA = RA_{H2} / RA_{ref}$

Steels with higher strengths or higher carbon contents are generally considered critical and are therefore mainly used in static applications of appropriate dimensioning.
Similarly, steels with martensitic microstructure show considerably lower RRA values than austenitic steels, as shown in Fig. 6.

Choice of steel grade

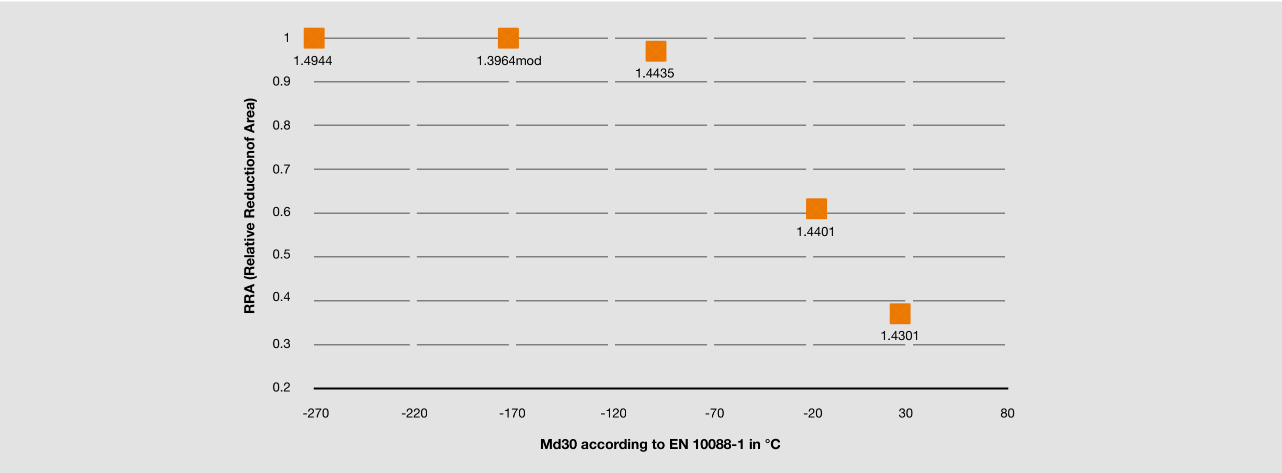

Fig.5 Effect of chemical composition acc. to Md_{30} on the relative reduction of area (RRA) for austenic stainless steels

The right choice of material is crucial

Depending on the requirements, stainless steels or engineering steels can be used.

Generally spoken, the more stable the austenite, the higher the RRA.

The stability of austenite against strain induced martensite is often given by Md_{30} which is defined as the lowest temperature at which 50 vol.% of austenite is transformed at a plastic (true tensile) strain of 30% into α'-martensite. The relation between Md_{30} and chemical composition is described with a formula in various standards, such as EN 10088-1:

Md_{30} = 551 - 462(C+N) - 9.2Si - 8.1Mn - 13.7Cr - 29(Ni+Cu) - 18.5Mo - 68Nb

With increasing Md_{30}, RRA shows a sharp decrease above -100°C (see fig. 5).

For stainless steels, Acidur®4435H2 / UGI®4435H2 is currently the standard solution. For demands for higher yield strengths requirements, Acidur®3964H2 / UGI®209H2, Magnadur®601H2 and UGI®4944H2 are recommended.

The newly developed Acidur®4636H2 displays similar properties as Acidur®4435H2 / UGI®4435H2 yet involving less expensive alloying elements.

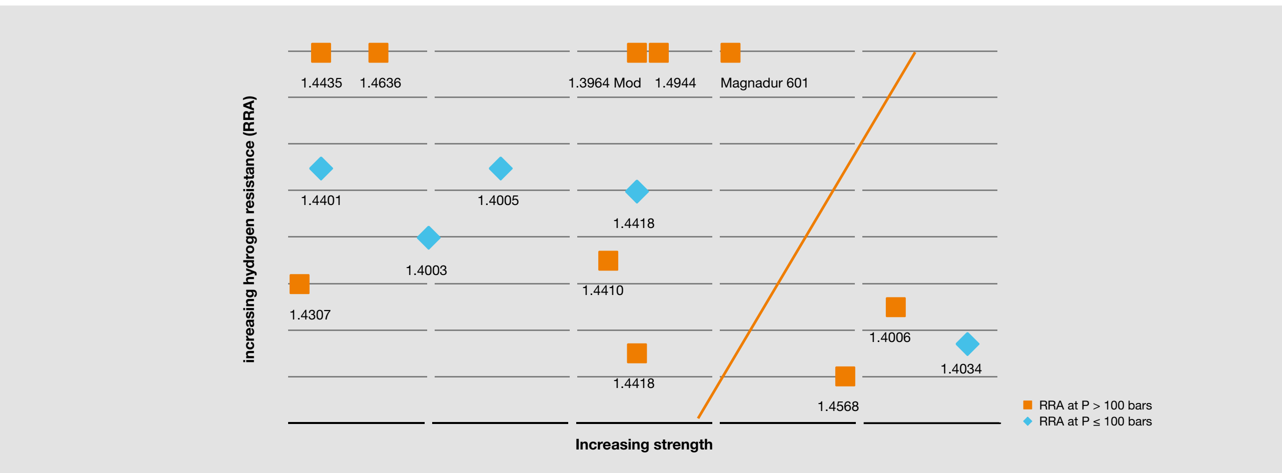

Fig.6 Selecting guide for the choice of steel grade

Characteristics of selected steels

The austenitic steels presented below are suitable for tank valves and sensors in fuel cells, as well as for valves in electrolyzers in hydrogen production.

Acidur®4435H2 / UGI®4435H2

is a steel of low strength and good ductility. Already well-known for its good corrosion resistance, it is also highly resistant to hydrogen embrittlement even after cold working.
Due to its precipitation free microstructure, it displays very good weldability.
Condition as-supplied: A* / HS**
Ø 2 - 200 mm, 3 - 6 m, peeled or cold drawn
*A: solution annealed
**HS: high strength condition: cold drawn or strain-hardened

Acidur®4636H2

provides similar characteristics as Acidur®4435H2 / UGI®4435H2, but being a low-nickel alloy, it is considered to be an economical alternative.
Condition as-supplied: solution annealed (A)
Ø 35 - 235 mm, 3 - 10 m; peeled

Acidur®3964H2 / UGI®209H2

Due to finest precipitates after solution annealing, these steels are characterized by increased strength combined with good toughness properties. Cold forming increases the strength while maintaining the good toughness properties.
In both strength levels, this steel is uncritical regarding hydrogen embrittlement; only the weldability is slightly reduced in the cold-formed condition.
Condition as-supplied: A / HS:
Ø 20 - 250 mm, 3 - 10 m; peeled (A)
Ø 20 - 210 mm, 8 - 10 m; peeled (HS)

Magnadur®601H2

This steel shows an excellent combination of high strength and high toughness properties, along with very good corrosion behavior:
It is highly resistant to hydrogen embrittlement and stress corrosion cracking.
Condition as-supplied: HS (strain-hardened)
Ø 50 - 235 mm, 8 - 10 m, peeled

UGI®4944H2

A precipitation hardening steel, which displays a good combination of strength and toughness properties and a very good resistance against hydrogen embrittlement. This steel also features high corrosion resistance at elevated temperatures and shows a stable austenitic structure at cryogenic temperature.
Condition as-supplied: annealed & aged
Ø 16 - 50 mm, 3.3 m, peeled and polished

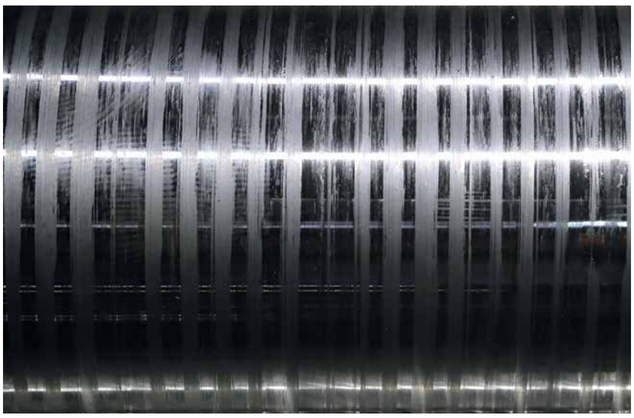

Fig. 7 peeled surface finish

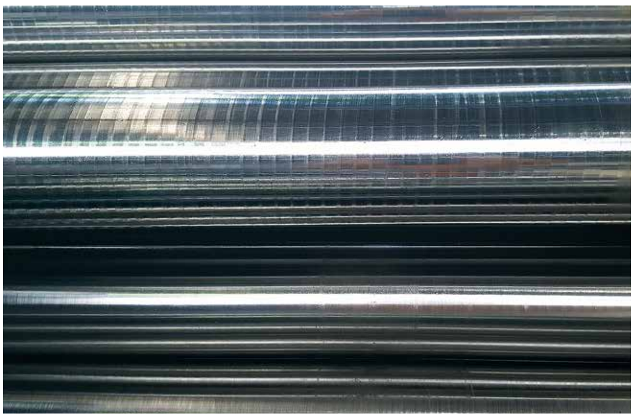

Fig. 8 polished surface finish

Technical data of selected steels

Brand	EN 10088-3	UNS	JIS	AISI ASTM A479
Acidur®4435H2 **UGI®4435H2**	1.4435	S31603	SUS316L	316L
Acidur®3964H2 **UGI®209H2**	1.3964 Mod 1.4681	S20910	–	XM-19
Acidur®4636H2	1.4636	–	–	–
Magnadur®601H2	–	–	–	–
UGI®4944H2	1.4944	S66286	SUH660	660

Chemical composition

Brand	C	Si	Mn	P	S	Cr	Mo	Ni	N	Others
Acidur®4435H2 **UGI®4435H2**	≤ 0.03	≤ 1.0	≤ 2.0	≤ 0.045	≤ 0.030	17.0 - 18.0	2.5 - 3.0	12.5 - 14.0	≤ 0.1	
Acidur®3964H2 **UGI®209H2**	≤ 0.06	≤ 1.0	4.0 - 6.0	≤ 0.045	≤ 0.030	20.5 - 23.5	1.5 - 3.0	11.5 - 13.5	0.2 - 0.4	Nb: 0.1 - 0.3 V: 0.1 - 0.3
Acidur®4636H2	≤ 0.06	≤ 0.5	12.0 - 13.0	≤ 0.035	≤ 0.035	17.0 - 18.0	≤ 0.75	7.5 - 10.5	≤ 0.10	Cu: 2.5 - 3.5
Magnadur®601H2	≤ 0.05	≤ 0.3	18.0 - 20.0	≤ 0.030	≤ 0.005	15.5 - 17.5	2.0 - 2.8	4.2 - 5.0	0.4 - 0.5	
UGI®4944H2	≤ 0.08	≤ 1.0	≤ 2.0	≤ 0.025	≤ 0.025	13.5 - 16.5	1.0 - 1.5	24.0 - 27.0	–	Ti: 1.9 - 2.35 V: 0.1 - 0.5

Mechanical properties

Brand	Condition	**Rp 0.2 / YS** MPa / ksi	**Rm / UTS** MPa / ksi	**A5d / A4d** %	**Z / RA** %
Acidur®4435H2 **UGI®4435H2**	Annealed High strength	≥ 240 / 35 ≥ 400 / 58	≥ 515 / 75 ≥ 600 / 87	≥ 40 / 42 ≥ 20 / 21	≥ 55 ≥ 50≪
Acidur®3964H2 **UGI®209H2**	Annealed High strength	≥ 380 / 55 ≥ 725 / 105	≥ 690 / 100 ≥ 930 / 135	≥ 35 / 37 ≥ 20 / 21	≥ 55 ≥ 50≪
Acidur®4636H2	Annealed High strength	≥ 240 / 35 ≥ 400 / 58	≥ 515 / 75 ≥ 600 / 87	≥ 40 / 42 ≥ 20 / 21	≥ 55 ≥ 50≪
Magnadur®601H2	High strength	≥ 965 / 140	≥ 1035 / 150	≥ 20 / 21	≥ 50
UGI®4944H2	Annealed & aged	≥ 600 / 87	≥ 900 / 130	≥ 16 / 17	≥ 35

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