Special steel solutions for hydrogen technology

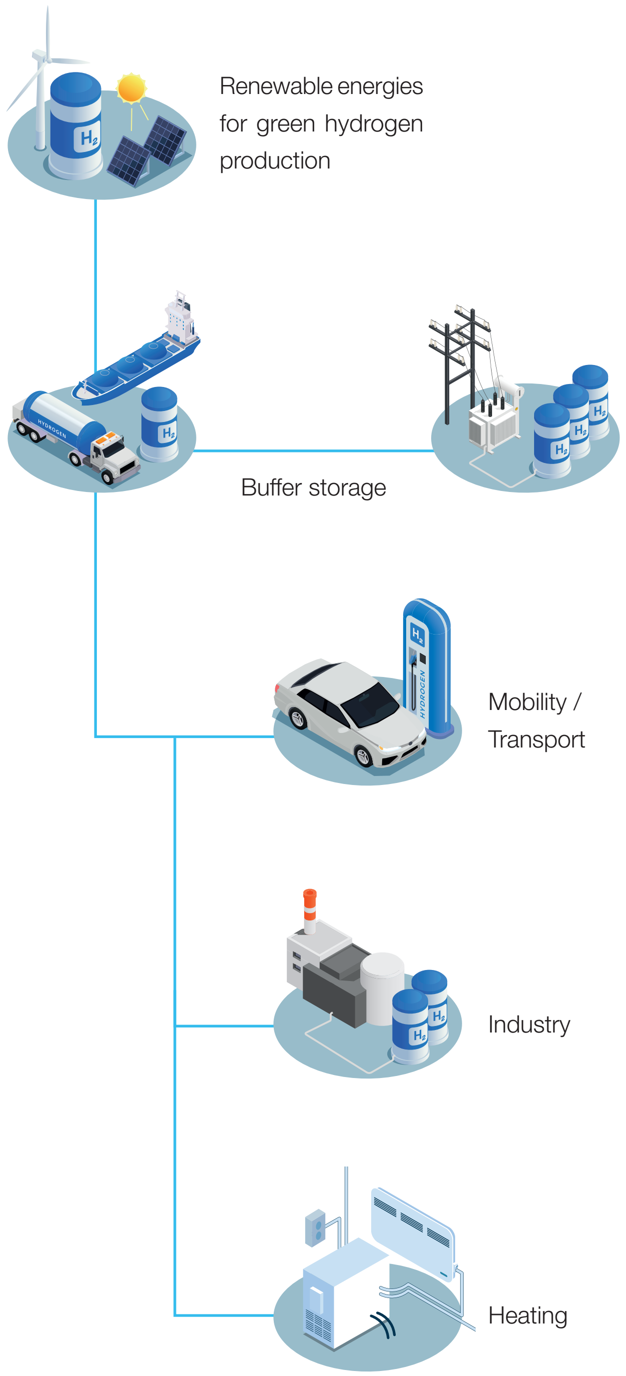
Swiss Steel Group

With hydrogen towards carbon 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 plays an important role in the transformation process towards climate neutrality.

- Swiss Steel Group is committed to climate protection and supports measures to reduce greenhouse gas emissions at its own production plants.
- The steels produced by the German and French Swiss Steel Group steel mills will support this demanding transformation process alongside the company's own future use of hydrogen as a process gas.



Unlike other renewable energies, hydrogen must be extracted from natural resources.

The best known and most commonly method for hydrogen separation is probably electrolysis, performed in large electrolyzers. The energy required for this operation is preferably supplied by "green" electricity sources as wind or solar energy.

Once the hydrogen has been produced, it is transported to its destination, using either large tanks or appropriately designed pipelines.

At its final destination, the hydrogen has to be stored before it can be used.

Hydrogen will be needed in different ways :

- In the field of mobility, hydrogen will be used in fuel cell technology or in combustion engines. Both technologies require tanks to supply hydrogen.
- Hydrogen as a process gas requires different prerequisites from those for mobility. Due to the significantly quantities of hydrogen required for the process, pipeline networks are more likely to be used in this case. However, as an industrial 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.

! Document not contractually binding. See disclaimers at back cover page of this document.

Production, Storage and Use of H_2

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

Hydrogen is also suitable as an energy storage medium and can then be converted back into electricity. However, these transformations involve high conversion losses, which have so far prevented significant economic use.

Demand for special steels

It is well known that hydrogen could impact the toughness properties of steel, causing what is known as hydrogen embrittlement.

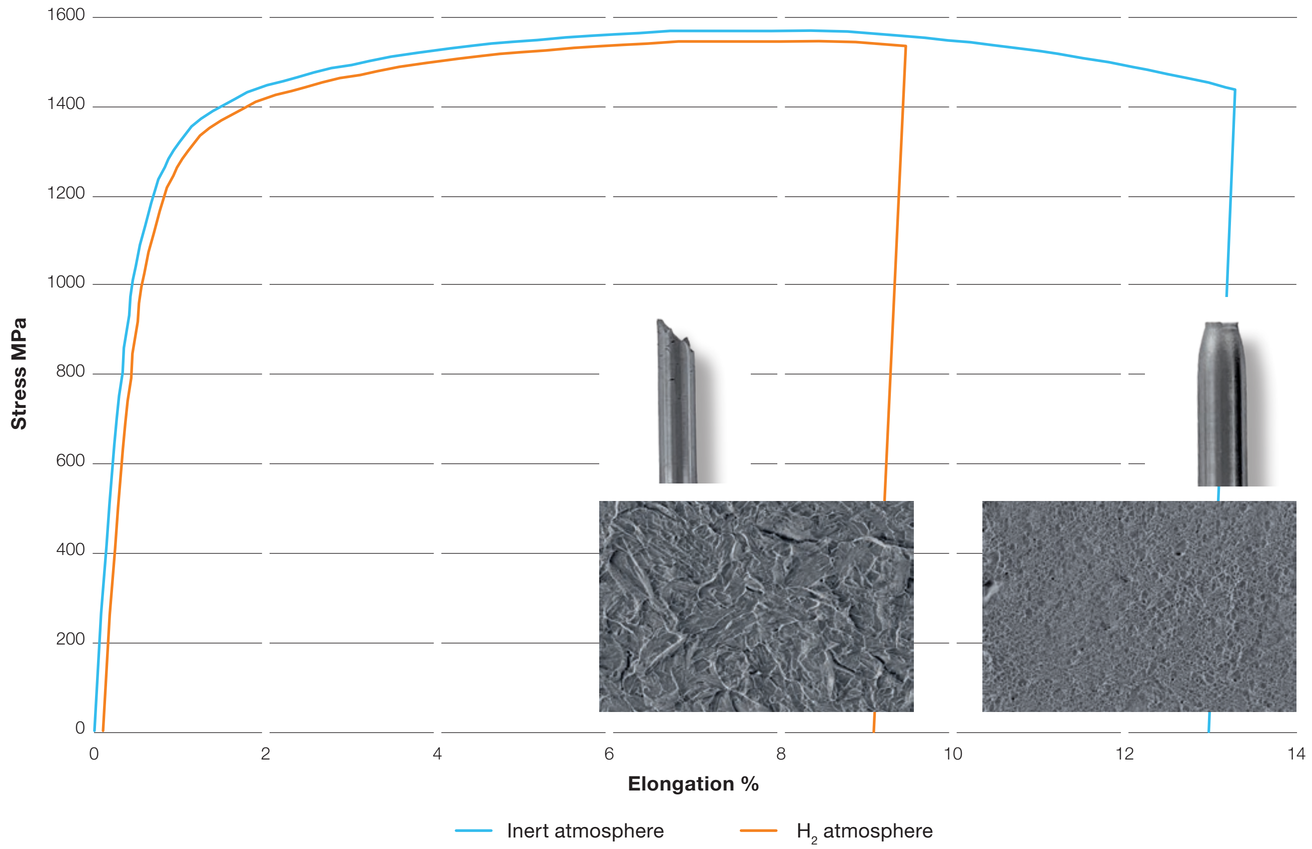
As a rule, the tendency to embrittlement is significantly lower on austenitic stainless steels. These steels are commonly used for tanks, pressure cylinders and fittings. Production, transport and storage of hydrogen require high pressures, which facilitate the diffusion of hydrogen and thus increase the risk of embrittlement.

A compromise must be found between high mechanical properties and good resistance to hydrogen embrittlement:

New steel grades must be developed and already established steels tested for their suitability in hydrogen environments.

Fig. 1 shows the influence of hydrogen on the mechanical properties in the tensile test as an example for an engineering steel.

Fig. 1 - Influence of hydrogen on the mechanical properties



Choice of steel

In a pressurized hydrogen atmosphere, the ductility properties such as elongation at fracture and reduction of area (RA) are significantly reduced.

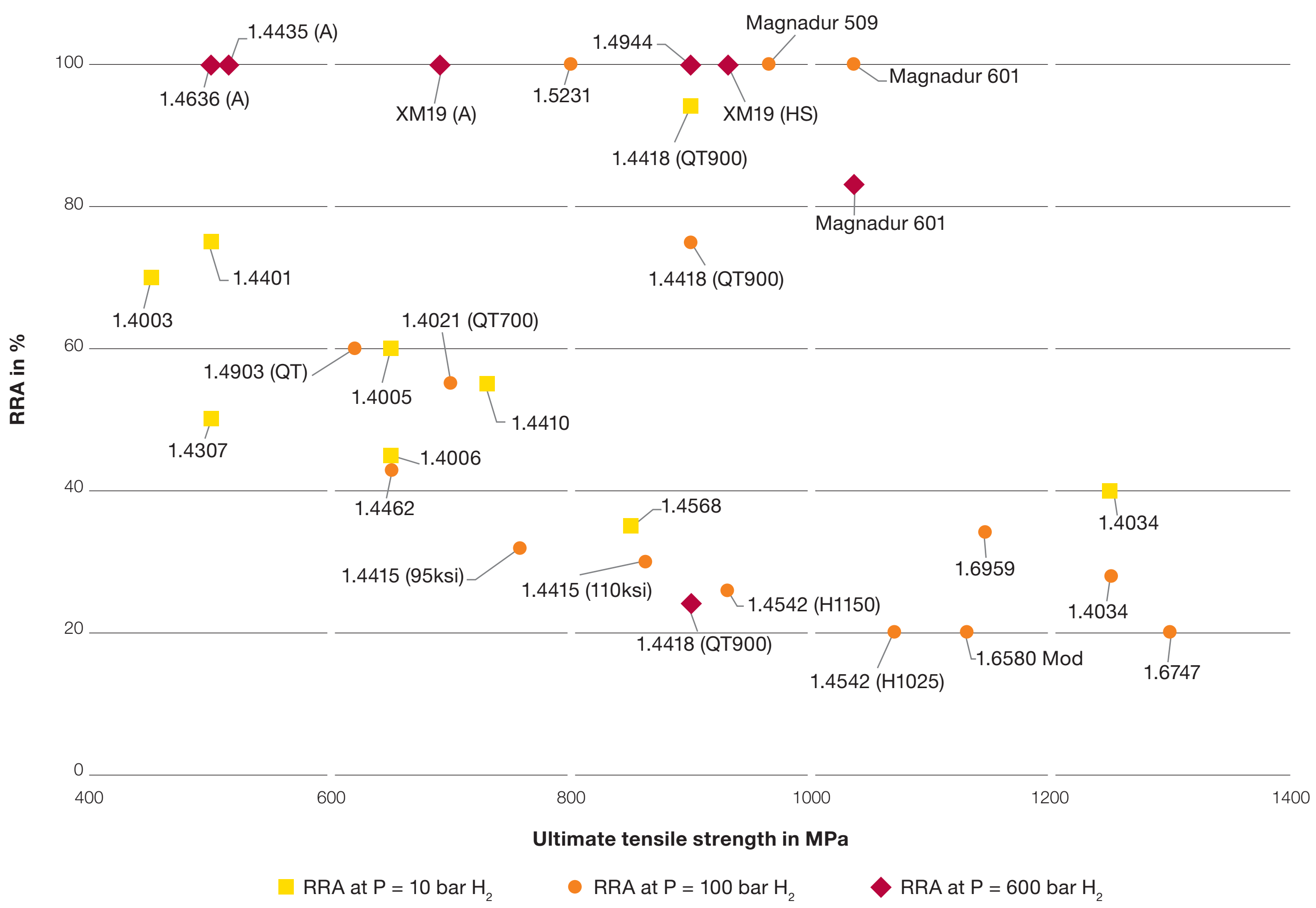
The yield strength and tensile strength are only slightly affected by hydrogen. The lower the strain rate in the test, the stronger the effect of hydrogen on the mechanical properties. This test under pressurized hydrogen is therefore carried out at the lowest possible strain rates.

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 atmosphere generally Helium: RRA = RA_{H2} / RA_{He}

Martensitic microstructures are generally more sensitive than austenitic materials when used in a hydrogen atmosphere as shown in Fig. 2.

Fig. 2 - RRA vs. UTS of selected steels at different H_2-pressure levels



Steels with higher strengths or higher carbon contents are generally considered critical and are therefore mainly used in static applications with appropriate dimensioning.

Carbon steel are often chosen for low H_2 pressure environment or for thick wall application like storage tanks; for example 42CrMo4 (1.7225).

For stainless steels, Acidur® 4435H2 / UGI® 4435H2 is currently the standard solution; for demands for higher yield strengths, Acidur® XM-19H2 / UGI® XM-19H2 and Magnadur® 601H2 are recommended.

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

UGI® 202NH2 is also an economical alternative which remains completely non-magnetic at cryogenic temperature and even after a high amount of cold work.

! Document not contractually binding. See disclaimers at back cover page of this document.

Demand for special steels

In the context of production, use and storage of pure hydrogen, the current testing of suitable steels by means of (slow strain) tensile tests is not sufficient since the influence of pressure is not taken into account.

Work is therefore underway to establish a standardized test (ISO EN 7039). The main point of this test is a modified specimen design in which the internal bore of the specimen is standardized (see Fig. 4).

Unlike the tensile test described in the previous section, the influence of pressurized atmosphere can be investigated. This test is particularly important for the use of valves, nozzles and pipelines.

Fig. 3 - Principle of high-pressure gaseous medium test method with hollow test pieces and schematic of basic system (non-safety related).

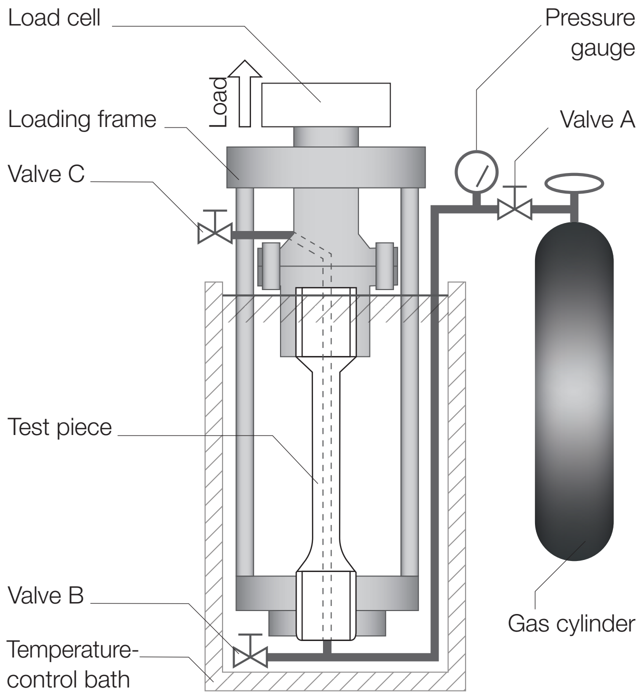


Fig. 4 - Hollow specimen for SSRT tests

Welding consumables for H_2 applications

Filler wires suitable for welding austenitic grades in hydrogen environment using MIG or TIG processes are mainly 316L grades.

- UGIWELD® 316LT or 316LM are adapted for Acidur® and UGI® 4435H2, Acidur® and UGI® XM-19H2 and Acidur® 4636H2.
- UGIWELD® 316LM with its high Silicon content is well adapted to MIG welding as UGIWELD® 316LT to TIG welding.

	AWS A5.9	ISO 14343-A	C	Si	Mn	Cr	Mo	Ni	N
UGIWELD® 316LT	ER316L	19 12 3 L	≤ 0.03	≤ 0.65	1.0 - 2.5	18.0 - 20.0	2.5 - 3.0	11.0 - 14.0	≤ 0.1
UGIWELD® 316LM	ER316LSi	19 12 3 L Si	≤ 0.03	0.65 – 1.0	1.0 – 2.5	18.0 – 20.0	2.5 - 3.0	11.0 – 14.0	≤ 0.1

Additive manufacturing powders and wires

Swiss Steel Group offers a wide range of products suited to additive manufacturing:

- Printdur powders used in SLM (Selective Laser Melting) processes guarantee excellent flow characteristics and low oxygen content.
  Available stainless steel powders are Printdur 316L, 17-4PH and 15-5PH.
- UGIWAM® wires used in WAM (Wire Additive Manufacturing) processes have a controlled lubricant layer weight which allows to reach deposition rates around 5 kg/h.
  Available stainless steel wires are UGIWAM® 304L, 316LSi, 17-4PH and 15-5PH

Characteristics of selected steels

Herein a choice of austenitic steel grades suitable for applications in fuel cells, valves and sensors as well as in electrolyzers and valves for hydrogen production.

Acidur® 4435H2 / UGI® 4435H2
is a steel of low strength and good ductility. Already well-known for its general corrosion resistance. It is also highly resistant against hydrogen embrittlement even after cold working. Due to its precipitation free microstructure, it displays very good weldability.

Condition as-supplied:

– A (solution annealed)

– Ø 10 - 200 mm, 3 – 6 m, peeled

Acidur® 4636H2
provides similar characteristics as Acidur® 4435H2 / UGI® 4435H2, but being a nickel – low alloy, it is considered to be an economical alternative.

Condition as-supplied:

– A (solution annealed)

– Ø 35 - 235 mm, 3 – 10 m; peeled

Acidur® XM-19H2 / UGI® XM-19H2
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 high toughness. 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 (solution annealed) / HS*

– Ø 20 - 250 mm, 3 – 10 m; peeled (A)

– Ø 20 - 210 mm, 8 – 10 m; peeled (HS*)

*HS: high strength condition: cold drawn or strain-hardened

UGI® 202NH2
is a 200 serie austenitic stainless steel, which represents an economical alternative to the 316L. With its high content in manganese and in nitrogen, UGI® 202NH2 is a totally non-magnetic at very low temperature and even after a high amount of cold work. Due to its austenite stability, UGI® 202NH2 is designed for cryogenic environments and for non-magnetic spring wires with no interference with electromagnetic waves.

Condition as-supplied:

– Spring wires: Ø 0,2 to 10 mm

– Bars: Ø 2 - 130 mm, 3 to 6 m; peeled or cold drawn

Magnadur® 509H2 & 601H2
these steels show an excellent combination of high strength and high toughness properties, along with very good corrosion behavior. They are highly resistant to hydrogen embrittlement and stress corrosion cracking.

Condition as-supplied:

– HS (Strain-Hardened)

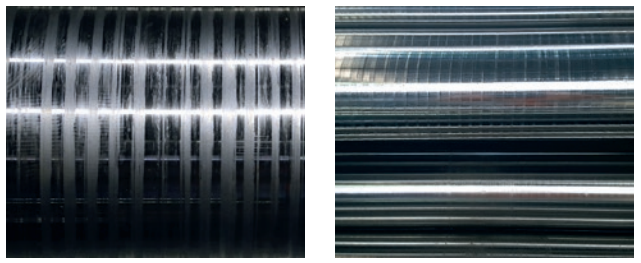
– Ø 50 - 235 mm, 8 – 10 m, peeled

UGI® 4944H2
A precipitation hardening austenitic 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 temperatures.

Condition as-supplied:

– Annealed & aged

– Ø 16 - 50 mm, 3,3 m, peeled and polished



Surface condition as supplied: peeled (left), peeled and polished (right)

Technical data of selected steels

Brand	EN 10088-3	UNS	JIS	AISI ASTM A479
Acidur® 4435H2 UGI® 4435H2	1.4435	S31603	SUS316L	316L
Acidur® XM-19H2 UGI® XM-19H2	1.3964 Mod 1.4681	S20910	-	XM-19
Acidur® 4636H2	1.4636	-	-	-
UGI® 202NH2	1.4374	S20200*	SUS202*	202*
Magnadur® 509H2	-	-	-	-
Magnadur® 601H2	-	-	-	-
UGI® 4944H2	1.4944	S66286	SUH660	660

* Except for Nitrogen

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® XM-19H2 UGI® XM-19H2	≤ 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
UGI® 202NH2	≤ 0.10	≤ 0.6	9.0 – 10.0	≤ 0.030	≤ 0.03	17.5 – 18.5	-	5.0 – 6.0	0.25 – 0.35	
Magnadur® 509H2	≤ 0.05	≤ 0.3	18.0 – 20.0	≤ 0.030	≤ 0.005	17.0 – 19.0	0.9 – 1.2	2.5 – 3.5	0.5 – 0.6	
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 / ROA %
Acidur® 4435H2	Annealed	≥ 240 / 35	≥ 515 / 75	≥ 40 / 42	≥ 55
UGI® 4435H2	High strength	≥ 400 / 58	≥ 600 / 88	≥ 20 / 22	≥ 50
Acidur® XM-19H2	Annealed	≥ 380 / 55	≥ 690 / 100	≥ 35 / 37	≥ 55
UGI® XM-19H2	High strength	≥ 725 / 105	≥ 930 / 135	≥ 20 / 22	≥ 50
Acidur® 4636H2	Annealed	≥ 240 / 35	≥ 515 / 75	≥ 40 / 42	≥ 55
	High strength	≥ 400 / 58	≥ 600 / 88	≥ 20 /22	≥ 50
UGI® 202NH2	Annealed	≥ 320 / 45	≥ 680 / 100	≥ 40 / 42	≥ 55
	Skin pass (free machining)	≥ 400 / 58	≥ 800 / 115	≥ 30 / 32	≥ 40
	Cold drawn (spring wire)	≥ 1400 / 220	≥ 1700 / 245	≥ 3 / 3	≥ 8
Magnadur® 509H2	High strength	≥ 965 / 140	≥ 1035 / 150	≥ 20 / 22	≥ 50
Magnadur® 601H2	High strength	≥ 965 / 140	≥ 1035 / 150	≥ 20 / 22	≥ 50
UGI® 4944H2	Annealed & aged	≥ 600 / 87	≥ 900 / 130	≥ 16 / 18	≥ 35

Document not contractually binding. See disclaimers at back cover page of this document.

Swiss Steel Group

hydrogen@swisssteelgroup.com
www.swisssteel-group.com

The information and data presented here in are typical or average values and are not a guarantee of maximum or minimum values. Only the information reported on our material certificates is to be considered as relevant. Applications specifically suggested for material described herein are made for the purpose of illustration only to enable the reader to make its own evaluation and are not intended as warranties, either express or implied, of fitness for any purposes.

Villi® - www.imprimerie-villiere.com
H2 with DEW_EN – 05-2024
D241546EN