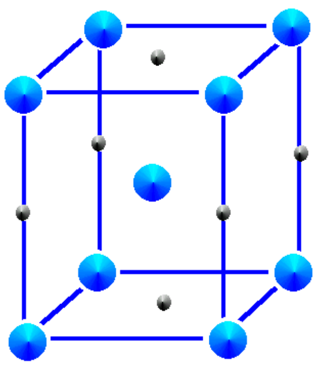
Martensitic Stainless Steels

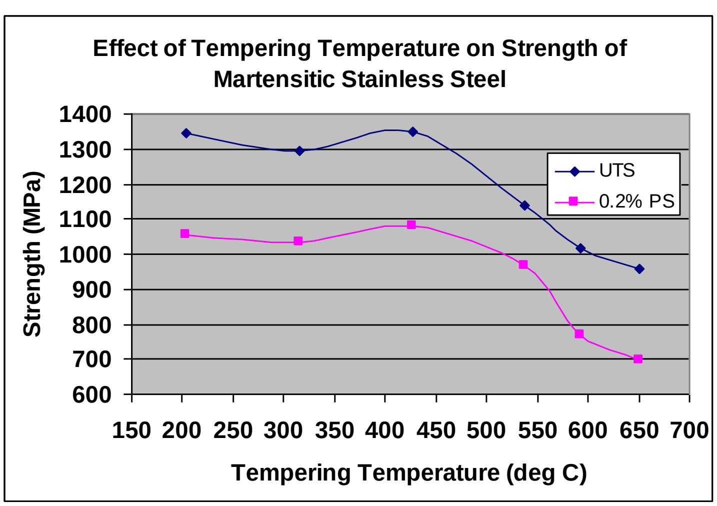
When we think of stainless steel the chances are that the first thing that springs to mind is an austenitic or ferritic application, in 304, 316, or 430. There has also been a lot of activity devoted to duplex stainless steels in recent years. Yet, it is worth remembering that Harry Brearley's original stainless steel was a martensitic type.

Martensitic stainless steels tend to be forgotten, perhaps because they are not made in large quantities compared with austenitic and ferritic grades. They are not as "exciting" as some of the newer duplex grades. However, martensitic stainless steels play a huge and often unseen part in our modern world. The intention of this short article is to remind us just how important they are.

Basic Metallurgy



Martensitic stainless steels work in the same way as many low alloy hardenable steels. Carbon is the key element. Normally, when steels are heated they transform from ferrite to austenite. On slow cooling the steel transforms back to ferrite. However, with fast cooling through quenching in water, oil, or sometimes even air, the carbon atoms become trapped and distort the normal body centred cubic, bcc, ferritic atomic matrix. This is known as body-centred tetragonal. The distortion of the atomic matrix leads to the hard martensitic structure. The higher the carbon level is, the greater is the distortion, and the harder is the resulting martensite. In the as-quenched condition, martensitic steels are virtually useless as they have insufficient impact toughness. Occasionally, lower carbon martensitic steels can be used in the as-quenched condition for wear resistance. The most usual treatment following quenching is tempering. Tempering involves heating the steel to somewhere between 200 and 700 deg. C. The temperature and length of time at temperature determines the final properties of the steel. Tempering imparts a useful combinations of strength and toughness.



The graph shows how the tempering temperature affects the strength of the steel.

Carbon levels can vary from less than 0.1% to over 1% in the martensitic stainless steels. In combination with other elements, this wide variation allows a wide range of properties to be developed for specific applications. In low alloy steels elements such as chromium, nickel and molybdenum are used to improve the "hardenability" of the steel. Hardenability is a measure of the maximum section size which will transform to martensite on cooling. This is related to the "ruling section". In stainless steels, chromium is present in large amounts and so have excellent hardenability. Nickel and molybdenum are also used. Mo has the added advantage of increasing the steel's corrosion resistance.

Mechanical Properties of Martensitic Grades

The European standard for long products EN 10088-3 has a wide range of martensitic grades, summarised in the table below. Machinable grades with sulphur are designated in red.

EN number	Generic Name	C	Cr	Mo	Ni	V	Max Dia (mm)	HT Condition	0.2% PS (MPa) min	UTS (MPa)	El (%) Min	Impact (J)
EN 10088-3 Standard Martensitic Grades												
1.4005	**416**	**0.06/ 0.15**	**12.0/ 14.0**				**160**	**+QT650**	**450**	**650/ 850**	**15**	**25**
1.4006	**410**	**0.08/ 0.15**	**11.5/ 13.5**				**160**	**+QT650**	**450**	**650/ 850**	**12**	**-**
1.4021	**420**	**0.16/ 0.25**	**12.0/ 14.0**				**160**	**+QT700**	**500**	**700/ 850**	**13**	**25**
							160	**+QT800**	**600**	**800/ 950**	**12**	**20**
1.4028	**420**	**0.26/ 0.35**	**12.0/ 14.0**				**160**	**+QT850**	**650**	**850/ 1000**	**10**	**15**
1.4031	**420**	**0.36/ 0.42**	**12.5/ 14.5**				**160**	**+QT800**	**650**	**800/ 1000**	**10**	**12**
1.4034	**420**	**0.43/ 0.50**	**12.5/ 14.5**				**160**	**+QT800**	**650**	**850/ 1000**	**10**	**12**
1.4419		**0.36/ 0.42**	**13.0/ 14.5**	**0.60/ 1.00**			**No properties defined in Quenched and Tempered condition**					
1.4116		**0.45/ 0.55**	**14.0/ 15.0**	**0.50/ 0.80**		**0.10/ 0.20**	**No properties defined in Quenched and Tempered condition**					

1.4110		0.48/ 0.60	13.0/ 15.0	0.50/ 0.80		≤ 0.15	No properties defined in Quenched and Tempered condition					
1.4104		0.10/ 0.17	15.5/ 17.5	0.20/ 0.60			60	+QT650	500	650/ 850	12	
							160				10	
1.4122		0.33/ 0.45	15.5/ 17.5	0.80/ 1.30			60	+QT750	550	750/ 950	12	20
							160					14
1.4057	431	0.12/ 0.22	15.0/ 17.0		1.50/ 2.50		60	+QT800	600	800/ 950	14	25
							160				12	20
							60	+QT900	700	900/ 1050	12	20
							160				10	15
1.4313	F6NM	0.05 max	12.0/ 14.0	0.30/ 0.70	3.5/ 4.5		160	+QT700	520	700/ 800	15	70
							250				12	50
							160	+QT780	620	780/ 980	15	70
							250				12	50
							160	+QT900	800	900/ 1100	12	50
							250				10	40
1.4418		0.06 max	15.0/ 17.0	0.80/ 1.50	4.0/ 6.0		160	+QT760	550	760/ 960	16	90
							250				14	70
							160	+QT900	700	900/ 1100	16	80
							250				14	60
EN 10088-3 Special Martensitic Grades												
1.4029		0.25/ 0.32	12.0/ 13.5				160	+QT850	650	850/ 1000	9	
1.4035		0.43/ 0.50	12.5/ 14.0				No properties defined in Quenched and Tempered condition					

1.4109		**0.60/ 0.75**	**14.0/ 16.0**	**0.40/ 0.80**			**No properties defined in Quenched and Tempered condition**					
1.4123		**0.35/ 0.50**	**14.0/ 16.0**	**1.00/ 2.50**		**1.5 max**	**No properties defined in Quenched and Tempered condition**					
1.4125	**440C**	**0.95/ 1.20**	**16.0/ 18.0**	**0.40/ 0.80**			**No properties defined in Quenched and Tempered condition**					
1.4112	**440B**	**0.85/ 0.95**	**17.0/ 19.0**	**0.90/ 1.30**		**0.07/ 0.12**	**No properties defined in Quenched and Tempered condition**					
1.4415		**0.03 max**	**11.5/ 13.5**	**1.50/ 2.50**	**4.5/ 6.5**	**0.10/ 0.50**	**160**	**+QT750**	**650**	**750/ 900**	**18**	**100**
								+QT850	**750**	**850/ 1000**	**15**	**80**

Some interesting points can be concluded from this table:

1. 1.4005 (416). This is the standard free-machining martensitic grade with sulphur. Millions of small components have been machined from this grade. Note that there is no EN equivalent to 416Se which uses selenium as the free-machining element.

2. Note the series of 12% chromium with increasing levels of carbon from 1.4021 to 1.4034. Note the increased strength coupled with loss of impact toughness.

3. Grade 1.4057. This is the nearest equivalent to the old BS 970 431S29. This grade is very commonly used, having an excellent combination of strength, toughness and corrosion resistance. The nickel content gives improved hardenability and impact toughness compared to the straight chromium steels. In many cases, the old BS 970 grade in condition T is still specified due to its higher nickel content of 2.0-3.0%, giving better properties.

4. 1.4313 and 1.4418. These low carbon martensitic grades have the benefit of being more weldable than other martensitic grades. Poor weldability is normally seen as a downside of martensitic steels due to their generally high carbon content, which requires pre and post heat treatment in welding. These steels are much better in this respect.

5. In many cases, in particular the very high carbon grades, the standard does not attempt to specify the mechanical properties which can be achieved in the hardened and tempered condition. The reason for this is not clear as the whole purpose of these steels is to provide high hardness usually for wear resistance. For these steels other sources of information must be consulted. For example, what kind of properties can be obtained from the highest carbon content of all the grades 1.4125 (440C). One

convenient source of information is on the AZOM (A to Z of Materials) Website www.azom.com.

Table 2. Mechanical properties of 440C grade stainless steels.

Tempering Temperature (°C)	Tensile Strength (MPa)	Yield Strength 0.2% Proof (MPa)	Elongation (% in 50mm)	Hardness Rockwell (HR C)	Impact Charpy V (J)
Annealed*	758	448	14	269HB max#	-
204	2030	1900	4	59	9
260	1960	1830	4	57	9
316	1860	1740	4	56	9
371	1790	1660	4	56	9
* Annealed properties are typical for Condition A of ASTM A276					
# Brinell Hardness is ASTM A276 specified maximum for annealed 440A, B and C.					

Courtesy of AZOM

We can now clearly see what sort of strength and hardness levels this material is capable of.

6. It is also true that standards tend to be conservative in the mechanical properties that can be achieved. Take for example, 431. The table below again from AZOM shows that much higher levels of strength can be obtained than would be implied by the EN standard alone. Of course, section size is important and these properties would only be achievable on small diameter bar.

Table 2. Mechanical properties of 431 grade stainless steels.

Tempering Temperature (°C)	Tensile Strength (MPa)	Yield Strength 0.2% Proof (MPa)	Elongation (% in 50mm)	Hardness Brinell (HB)	Impact Charpy V (J)
Annealed *	862	655	20	285 max	-
204	1345	1055	20	388	50
316	1295	1035	19	375	53
427	1350	1080	19	388	#
538	1140	965	19	321	#
593	1015	770	20	293	64
650	960	695	20	277	84
Grade 431 is frequently stocked and supplied in "Condition T", with specified tensile strength of 850 - 1000MPa.					
* Annealed tensile properties are typical for Condition A of ASTM A276; annealed hardness is the specified maximum. Grade 431 is only rarely stocked in annealed Condition A.					
# Due to associated low impact resistance this steel should not be tempered in the range 425-600°C					

Courtesy of AZOM

Of course, martensitic grades can also be obtained as flat products mainly for blades of various kinds. Most of the grades listed in EN 10088-3 are also found in EN 10088-2. Details of these can be found at https://bssa.org.uk/bssa_articles/ambient-temperature-mechanical-properties-of-martensitic-stainless-steel-flat-products-to-bs-en-10088-2/

The class of martensitic creep-resisting steels of the 1.49xx type are found in EN 10302. These are generally of the 9-12% CrMoV type often with additions of other elements such as niobium and tungsten. A summary of these steels can be found at https://bssa.org.uk/bssa_articles/chemical-composition-of-creep-resisting-steels-to-bs-en-10302/ Compositions https://bssa.org.uk/bssa_articles/ambient-temperature-mechanical-properties-of-creep-resisting-steels-to-bs-en-10302/ Properties

These steels are used in the power generation industry.

Corrosion Resistance of Martensitic Grades

The corrosion resistance of martensitic stainless steels is generally lower than that of the other types of stainless steel. However, with at least 11.5% chromium, they are genuine stainless steels giving a significantly improved corrosion resistance compared with low alloy steels. One only has to think of kitchen knives to realise that martensitic stainless steels are corrosion resistant in moderate conditions.

The higher Cr grades such as 1.4057 (431), 1.4122, and 1.4418 offer corrosion resistance just below, or comparable to that of 1.4301 (304) in many environments. No martensitic stainless steel can compare with 316 or higher grades for corrosion resistance.

Applications of Martensitic Stainless Steels

The combination of high strength, good toughness and moderate corrosion resistance allow martensitics to be used in a wide variety of applications including:

- Razor strip
- Blades and cutting tools
- Surgical instruments
- Gears
- Valves
- Pumps
- Shafts
- Offshore oil and gas components
- Bearings
- Mixers and stirrers
- Turbine parts
- Aerospace

Many of these applications are hidden to most of us which probably explains why martensitic stainless steels do not have a prominent public profile. It is good to remind ourselves that much of our modern world rests on martensitic stainless steels quietly doing their job behind the scenes.

Summary

Martensitic stainless steels have a long history stretching right back to Harry Brearley's invention in 1913. Their combination of strength, toughness and moderate corrosion resistance makes them ideal for a wide range of applications. Although not used in large quantities compared with austenitic and ferritic grades, they are a vital part of the stainless steel "armoury".