MLX®19

X1NiCrMoAlTi12-10-2

Ultra high-strength stainless steel

AUBERT&DUVAL

> THE INDUSTRIAL ENVIRONMENT

The use of Precipitation Hardening Stainless Steels for structural parts in industrial components has been in place for a while considering their superior environmental robustness. The pressure to use this type of martensitic stainless material has grown stronger and stronger due to the need to remove harmful protective coatings, such as chromates and cadmium, that are now on the list for removal under environmental legislation such as REACH in Europe.

Although a wide range of Precipitation Hardening Stainless Steels currently exists, it was not possible, until recently, to reach a tensile strength above 1850MPa (268ksi) with MLX®17 or Custom465®. In this field, for decades, the material selection for the structural components requiring the highest tensile strength has been only based on AISI 4340 and derivatives, including E35NiCrMo16 (819AW) and 300M. These low-cost materials provide excellent tensile strength, fatigue resistance, and good fracture toughness, but no corrosion resistance.

> MLX®19 STEEL GRADE DEVELOPMENT

Aubert & Duval has made major advances in improving the strength of high-performance corrosion-resistant steels, and MLX®19 is the first one. Precipitation Hardening Stainless Steel providing Ultra-High Tensile Strength in the range of 1900MPa (275ksi) for a Yield Strength higher than 300M (around 1785MPa, 259ksi). If the initial driver to develop MLX®19 has been structural aerospace components, other applications are now also targeted.

MLX®19 steel provides:

- Ultra-high hardenability
- Similar resistance to general corrosion as any other PH stainless grades (from 15-5PH to MLX®17)
- High Stress corrosion cracking (SCC) resistance

Because of its high resistance to corrosion, ultra-high strength and toughness combination, MLX®19 maraging steel is the best candidate in demanding landing gear without the use of toxic cadmium coatings.

Custom465® is a registered trademark of Carpenter Technology

> SPECIFICATIONS

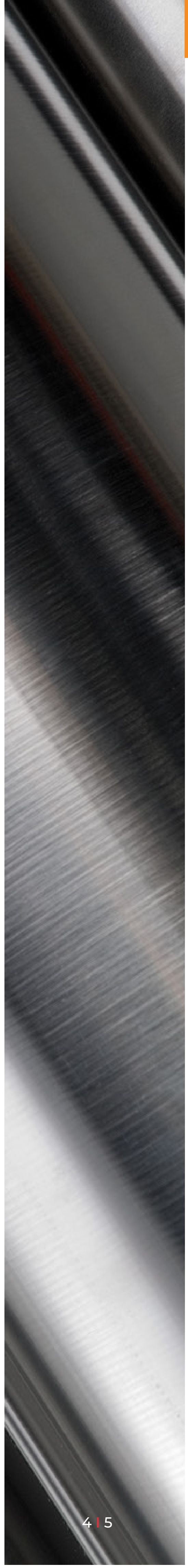
X1NiCrMoAlTi12-10-2
AMS: 5955 (bar and forging)
MMPDS allowable design data available from the 11th version
MLX®19 patent is pending (US8097098 / EP1896624)

> APPLICATIONS

Aerospace parts

Motorsport

Defense - Missiles



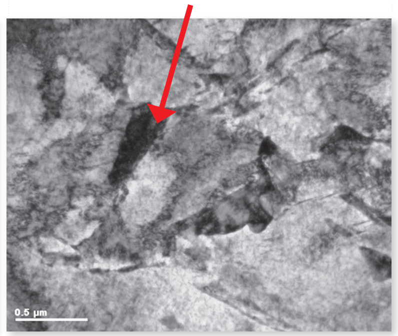
> CHEMICAL COMPOSITION (weight %)

	Cr	Mn	Si	P	S	Cr	Mo	Ni	Ti	Al	N
Mini	/	/	/	/	/	9.50	1.75	11.50	0.95	1.30	/
Maxi	0.02	0.25	0.25	0.015	0.010	10.50	2.25	13.00	1.50	1.70	0.01

Martensitic matrix (Cr, Mo)
↗ Corrosion resistance

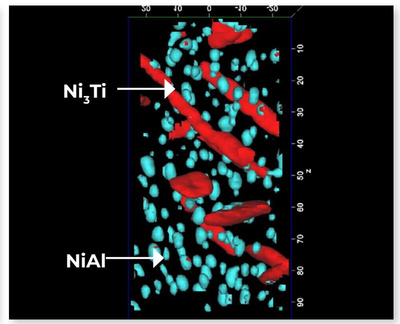
Martensitic matrix
(optical microscopy)

Austenite (Ni)
↗ K_{IC}



Austenite
(Transmission Election Microscopy)

Nanometric precipitates
↗ UTS



NiAl, Ni_3Ti precipitates
(Three-dimensional atom probe - 3-DAP)

Chromium and Molybdenum, in solid solution in the martensitic matrix, contribute to the corrosion resistance of MLX®19. After solution heat treatment and ageing, elements contributing to hard precipitates, are no longer in the matrix and the apparent percentage of Chromium increases to 12%, giving MLX®19 its good resistance to general corrosion in a salt brine environment or room chloride containing water for instance.

High Nickel content contributes in building reverse austenite phasis, highly favorable to achieve high toughness performances Nickel, Titanium and Aluminum percentages have been selected to achieve the best UTS/K_{IC} combination through the nanometric precipitates of Ni_3Ti and NiAl.

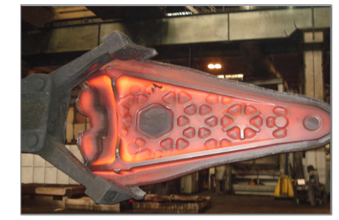
> PROCESS

MLX®19 steel is at least double vacuum melted (i.e., vacuum induction melted and then vacuum arc remelted or «VIM/VAR»), a triple melt option can be considered for the most stringent applications.

Melting, Remelting

Rolling

Open-die forging



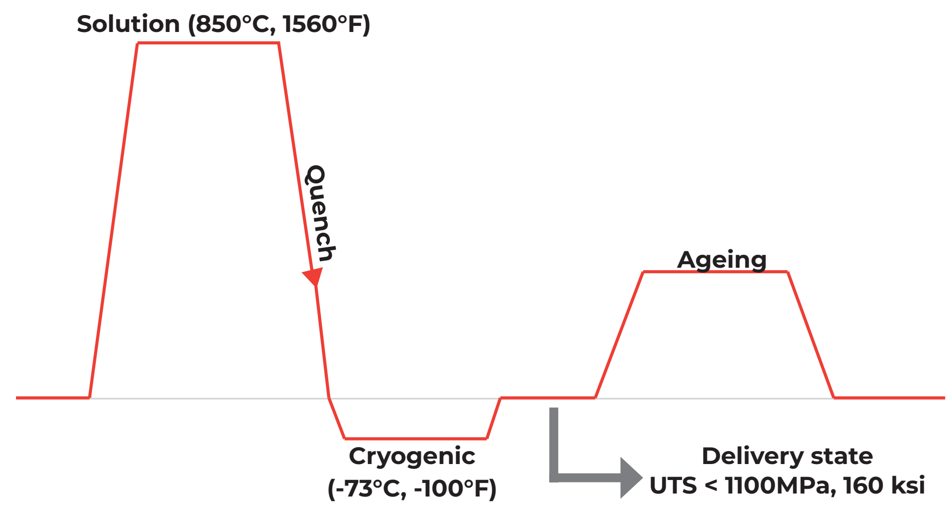
Closed-die forging

HEAT TREATMENT

Bars, wires, and forgings shall be solution heat treated by:

- Heating to 850°C ± 14°C (1560 °F ± 25°F), holding at temperature for 90 minutes ±15 min
- Quenching in oil, polymer or water
- Cooling to -73 °C (-100 °F) or colder, holding at that temperature for not less than 8 hours,
- Warming in air to room temperature.

We usually deliver the material in the solution heat treated condition, ready to be machined and aged.
We can also deliver the material in the natural state condition for forging stock.
The delivery in aged condition is currently not used by customers, considering the difficulty to machine at such a hardness level (> 51.5HRC)



> MAIN PHYSICAL PROPERTIES

Physical properties in SI units

Temperature	Thermal diffusivity	C Specific Heat	ω Density	K Thermal conductivity
°C	mm²/s	J/Kg.°C	Kg/cm³	W/m.°C
25	4.31	455	7719	15.1
70	4.45	481	7709	16.5
110	4.60	496	7697	17.6
150	4.71	511	7686	18.5
190	4.79	522	7675	19.2
230	4.88	534	7663	20.0
270	4.85	548	7651	20.3
310	4.90	565	7639	21.2
350	4,85	577	7627	21.4
390	4.72	594	7615	21.4
450	4.63	645	7597	22.7

Physical properties in U.S. units

Temperature	Thermal diffusivity	C Specific Heat	ω Density	K Thermal conductivity
°F	in²/s	Btu/lb.°F	lb/in³	Btu.hr-1.ft-1.°F-1
77	0.00667	0.1086	0.279	8.73
158	0.00689	0.1148	0.278	9.51
230	0.00713	0.1184	0.278	10.15
302	0.00729	0.1221	0.278	10.69
374	0.00742	0.1247	0.277	11.09
446	0.00756	0.1275	0.277	11.53
518	0.00751	0.1310	0.276	11.75
590	0.00760	0.1349	0.276	12.22
662	0.00751	0.1378	0.276	12.32
734	0.00731	0.1418	0.275	12.32
842	0.00718	0.1540	0.274	13.11

Mean coefficient of thermal expansion

Temperature from room temperature to indicated temperature		Mean coefficient of thermal expansion α	
°C	°F	10^{-6} m/m/°C	10^{-6} in/in/°F
230	110	10.96	6.09
302	150	11.16	6.20
374	190	11.38	6.32
446	230	11.61	6.45
518	270	11.83	6.57
590	310	11.99	6.66
662	350	12.13	6.74

> MACROSTRUCTURE

The segregation, as measured on billets, complies with the tightest requirements.

Class	Type	Severity
1	Freckles	A
2	White spots	A
3	Radial segregation	A
4	Ring pattern	B

Macrostructure according to ASTM A604

> CLEANLINESS

The segregation, as measured on billets, complies with the tightest requirements.

Type	A		B		C		D		A+B+C+D
	Thin	Heavy	Thin	Heavy	Thin	Heavy	Thin	Heavy	
Max	1	1	1.5	1	1	1	1.5	1	≤ 10

According to ASTM E 45 Method D (max levels and value on 160 mm² surface)

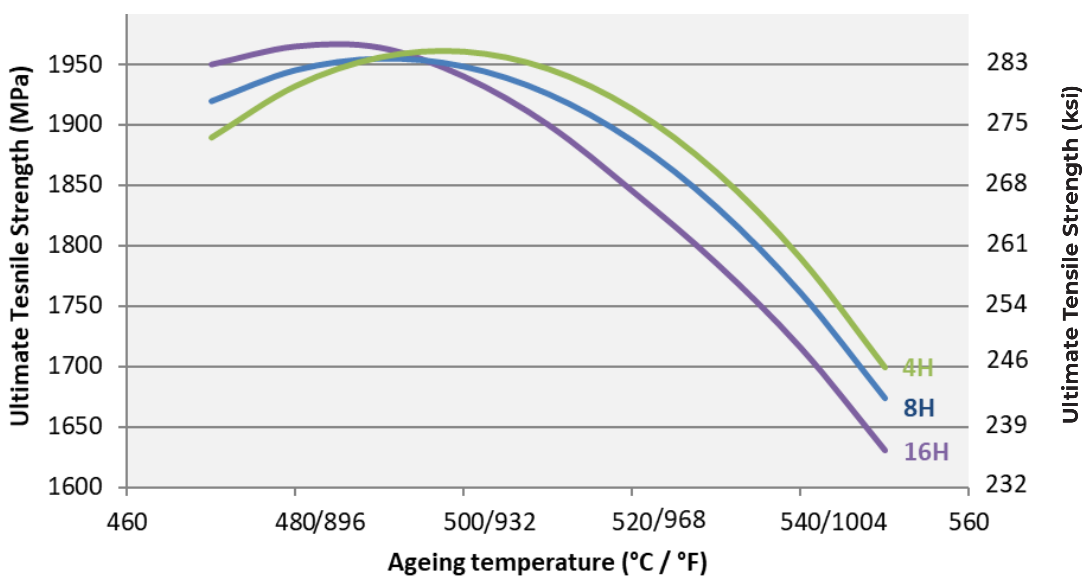
> EVOLUTION OF MECHANICAL PROPERTIES WITH AGEING TEMPERATURE

The typical ageing behavior of MLX®19 is given below, regarding evolution of Ultimate Tensile Strength, Yield Strength at 0.2% and fracture toughness with ageing time and temperature.

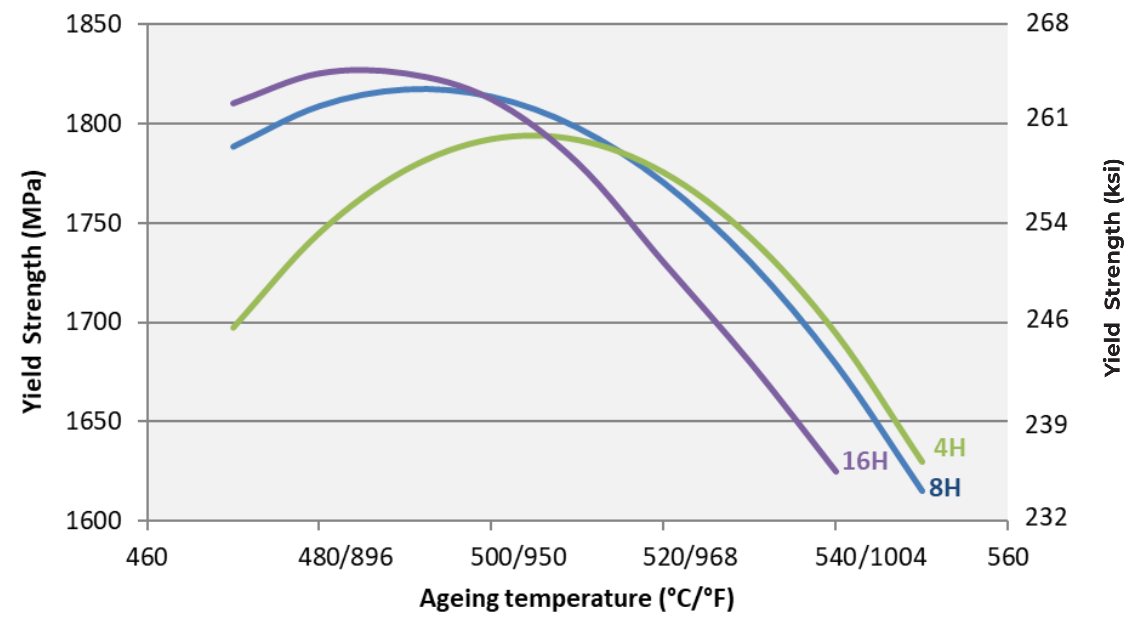
Solution heat treatment

- Heating to 850°C ± 14°C (1560 °F ± 25°F)
- Quenching in oil, polymer or water
- Cooling to -73 °C (-100 °F) for 8 hours

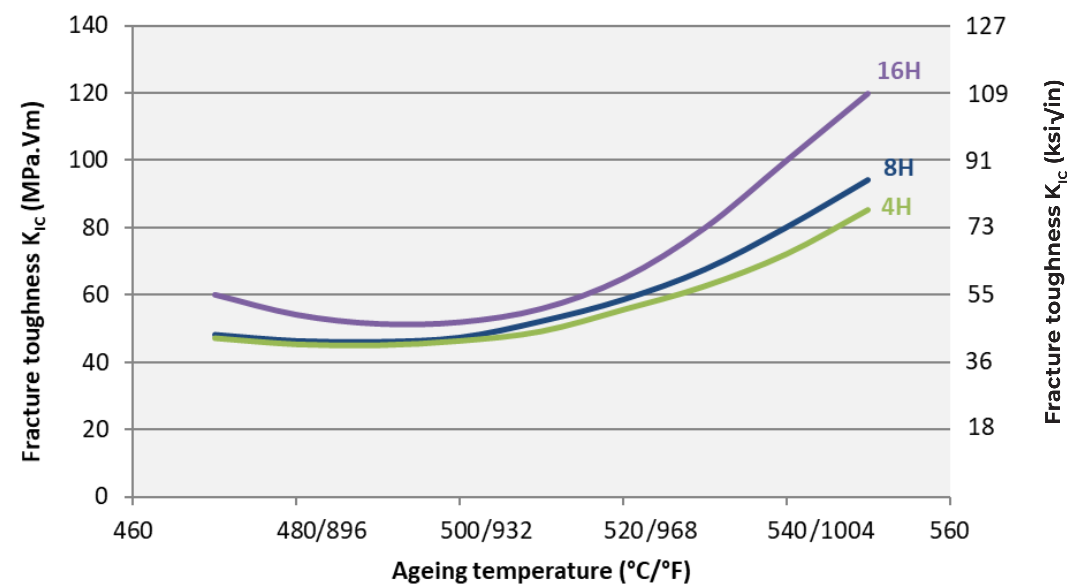
The following graphs show the typical properties determined in the longitudinal direction. Ageing was performed on coupons extracted from solution heat treated bars.



Properties depending on ageing time and temperature - UTS

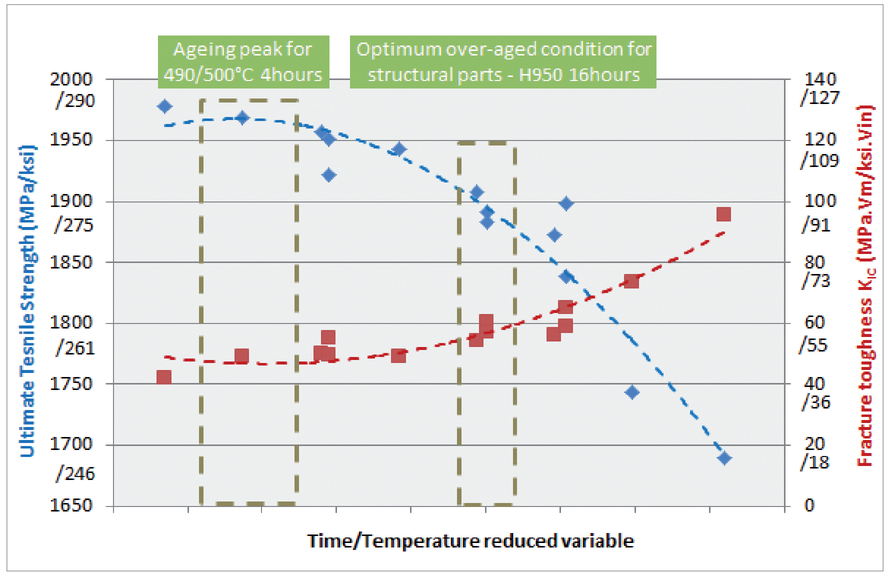


Properties depending on ageing time and temperature - YS0.2



Properties depending on ageing time and temperature - K_{IC}

Based upon this set of data, some fields of applications and types of processing can be recommended for MLX®19. In order to have a clear overview of the effect of ageing on properties, these values can be plotted using a reduced variable (Manson Coffin type) taking into account ageing time and temperature.



Combination of Ultimate Tensile Strength and Fracture Thoughness K_{IC}

AEROSPACE / DEFENSE

Ageing treatment dedicated to Aerospace or Defense structural parts must provide the best combination of tensile strength, damage tolerance and stress corrosion cracking properties. An over-aged condition must be selected to promote these properties.
Our recommendation is to use H950 for 16 hours. Results clearly highlight that this treatment is preferred compared with H1000 4 hours, giving poor tensile strength. AMS5955 and MMPDS design values have been defined and generated with this ageing treatment.

OTHER APPLICATIONS

For other applications, the ageing can be adapted based upon customer needs. For instance, for those requiring the highest strength possible, a treatment at the ageing peak is preferred. 490°C to 500°C (914°F to 932°F) for 4 hours must be targeted, giving the strongest material. A deep-freezing stage can be considered in some applications as optional as well. This will depend on the amount of retained austenite which can be tolerated and the selected ageing treatment.

Below are listed typical and minimum values of MLX®19 aged at H950 for 16 hours.

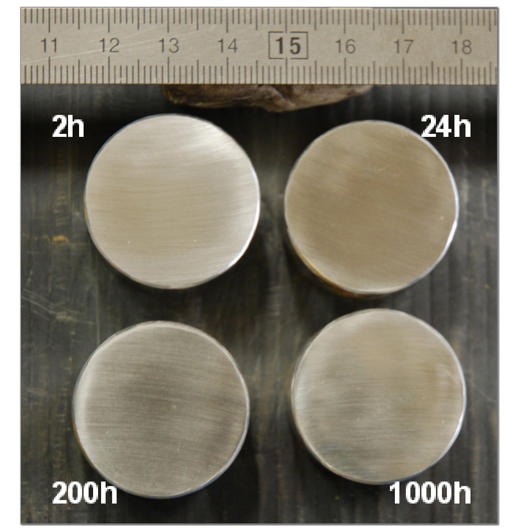
Ageing response being independent of the product size, tests conducted on coupons aged at the laboratory (extracted from bar after solution heat treatment/deep freezing) are fully representative of real cases (ageing on real parts).

H950 16 hours ageing	Direction	UTS (MPa) (ksi)	YS0.2 (MPa) (ksi)	A4d (%)	Reduced Area (%)	K_{IC} (MPa.√m) (ksi.√in)
AMS5955 min value	L (L-C)	1850 268	1715 249	9	40	45 41
	T (C-L)	1850 268	1710 248	7	35	/
MLX®19 Typical value	L (L-C)	1895 275	1785 259	11.8	50.8	54 49
	T (C-L)	1895 275	1783 259	10.2	43.9	49 45

> GENERAL CORROSION RESISTANCE

TEST CONDITIONS:

- Solution heat treatment: 850°C ± 14°C (1560 °F ± 14°F)
- Quenching in oil, polymer or water
- Cooling to -73 °C (-100 °F) for 8 hours
- Ageing: 510°C (H950) 16 hours



SALT SPRAY TEST:

Surface grinding in order to remove the small surface layer that was Chromium depleted following heat treatment (few hundreds of nanometers).

Passivation: Type 8 as per AMS 2700

Salt spray test as per ASTM B117.

When properly prepared as recommended above, the MLX®19 surface presents a general corrosion resistance similar with all the other Precipitation Hardened grades in the over-aged condition.

> MLX®19 / AISI 440C / 300M

TEST COMPARISON

This corrosion behaviour is far better than classical martensitic Corrosion RESistant (CRES) grades like AISI 440C. This makes MLX®19 the first and unique stainless grade suitable for Ultra High Strength applications.

MLX®19 – 1000 hours

AISI 440C – 286 hours

300M – 86 hours

> STRESS CORROSION

TEST CONDITIONS:

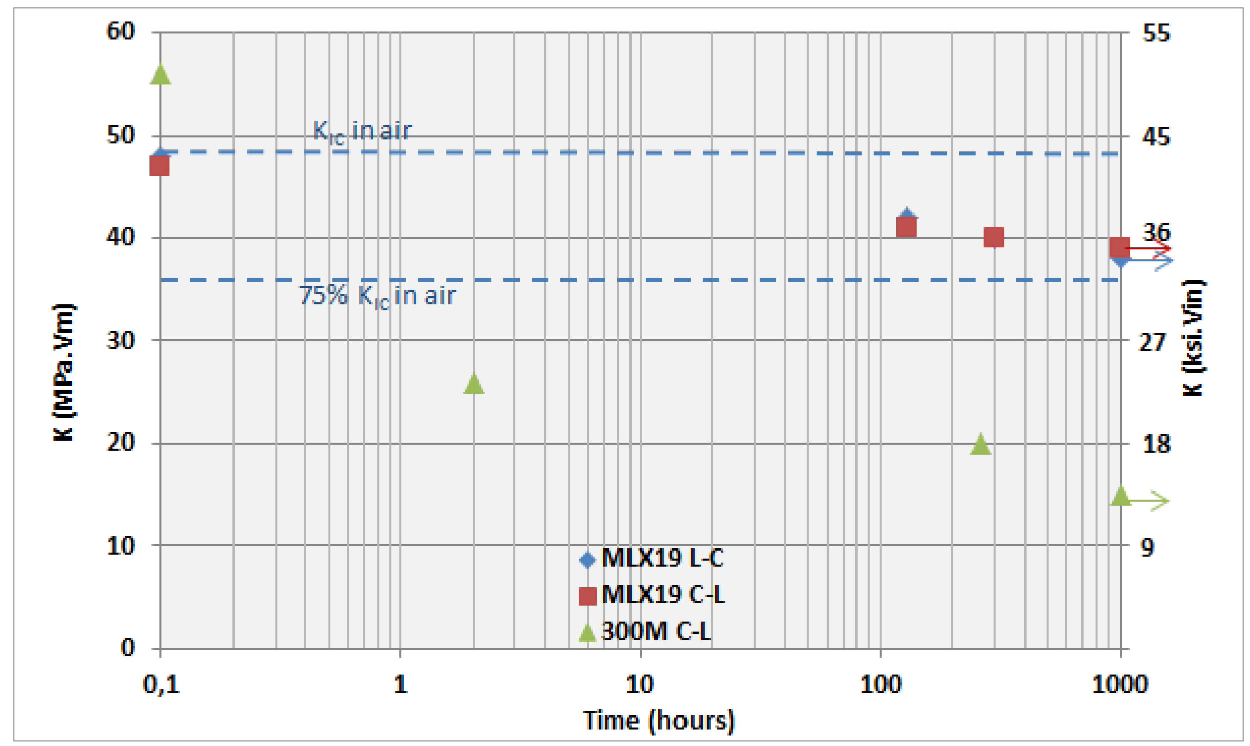
Solution heat treatment: 850°C ± 14°C (1560 °F ± 25°F), quenching in water, cooling to -73 °C (-100 °F) for 8 hours

Ageing: H950 16 Hours

Surface grinding in order to remove the small layer that was depleted of Chromium elements following heat treatment (few nanometers)

Stress corrosion cracking resistance performed according to ISO 7539-1 and ISO 7539-6

The main difference with the Rising Step Loading method is that the maximum load is applied all along the test.



Stress Corrosion Cracking resistance - K_{ISCC}

K_{ISCC} determined for MLX®19 is 80 to 90% of the K_{IC} value. As for K_{IC}, we cannot see any significant influence of crack orientation with grain flow. This K_{ISCC} values of MLX®19 are far better than those of 300M. For MLX®19, a minimum value of 75% of K_{IC} can be guaranteed (34MPa.√m).

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> FATIGUE PERFORMANCE

TEST CONDITIONS:

Solution heat treatment: 850°C ± 14°C (1560 °F ± 25°F), quenching in water, cooling to -73 °C (-100 °F) for 8 hours.

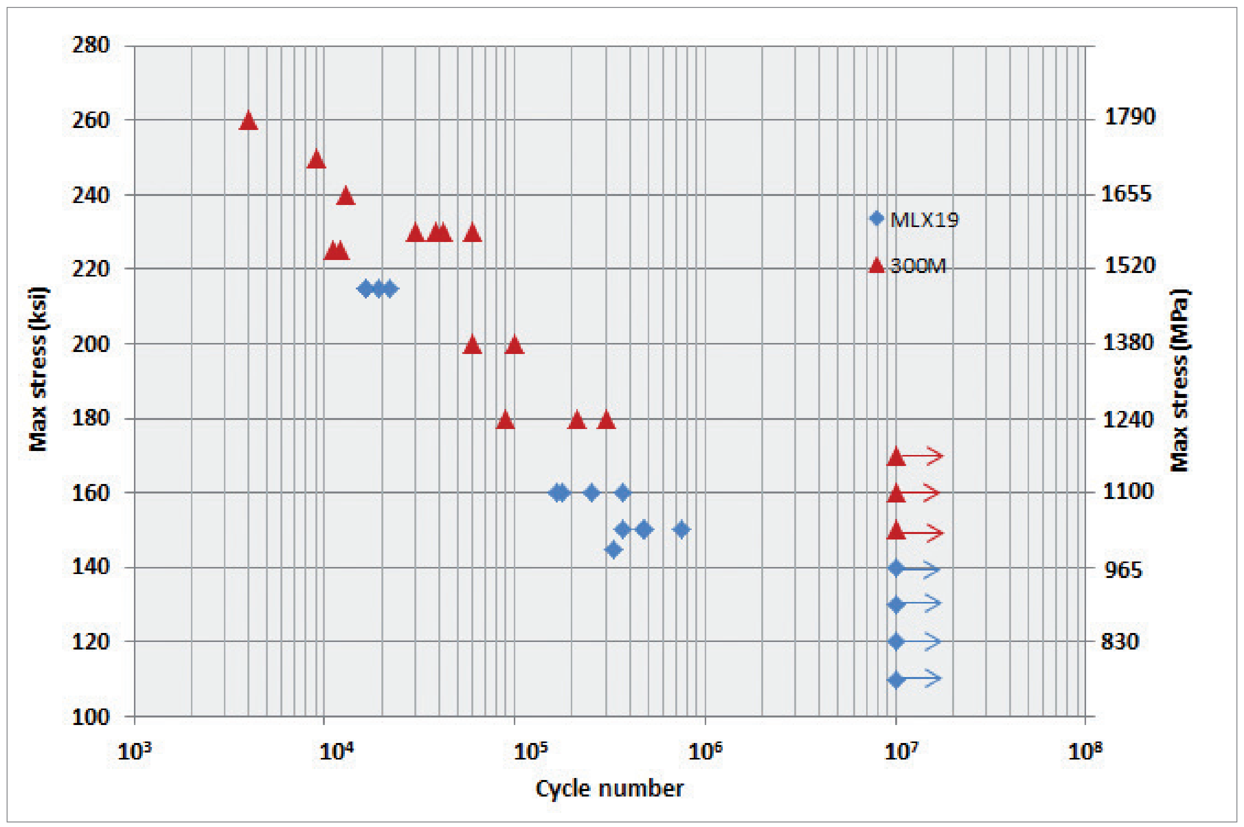
Ageing H950 for 16 hours, performed on coupons excised from solution heat treated bars.

Properties determined in longitudinal direction.

Axial fatigue with R=0,1.

Un-notched specimens, Kt=1,038 (preparation by machining in transverse direction and final grinding/polishing in longitudinal direction).

Test frequency: 15Hz.



S/N curve for R=0,1 (axial mode), Kt=1,038 (un-notched specimens), 15hz

Fatigue performance of MLX®19 is lower than 300M. Typical failure initiation is at a cleavage zone or starts at a Ti-C-N particle or both. This behavior is typical of any Ultra High Strength maraging steels hardened with a high amount of titanium and/or aluminum.
A few examples of applications are given in next pages.

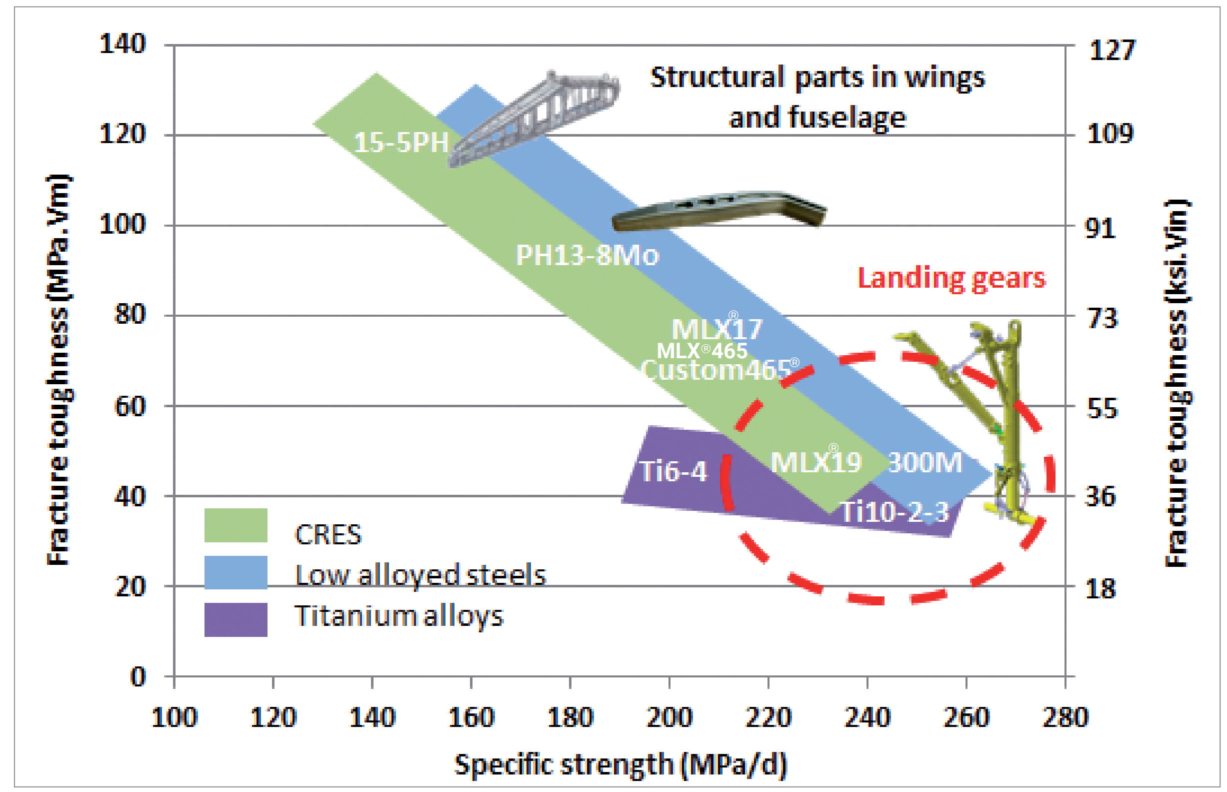
> APPLICATION IN AEROSPACE PARTS

TECHNICAL CHALLENGES FOR AEROSPACE PARTS

Critical aircraft structural parts used in extreme conditions require high performance materials. They are currently mainly made of low alloyed carbon steels, with surface coatings for corrosion resistance purposes.

These coatings require heavy maintenance procedures on aircraft in service, and some of them could be banned in the near future due to environmental regulations.

A solution to replace these steels is titanium alloys. They are used on some components of recent long range aircraft landing gear. However, costs and casing constraints are major issues for titanium alloys.



A substitute solution to titanium is based on high strength Corrosion RESistant steels (CRES) with the properties required by the aeronautic industry. MLX®19, recently developed and patented by Aubert & Duval, meets these requirements. The ambition is that landing gear components using this material will be more resistant to corrosion, allowing maintenance overhaul to be extended; thereby reducing operational costs. The landing gear will require fewer corrosion protection coatings and be compliant with the latest regulations, offering more potential cost saving for manufacturers.

EXISTING GRADE OFFER AND MLX®19 BENEFITS

A wide range of new steel grades has been developed in the last decades, all aiming to provide the ideal characteristics requested by landing gears part manufacturers.

Among them, MLX®19 is now the unique Corrosion RESistant (CRES) grade offering the best compromise of in-use properties and being a real candidate to substitute for the low alloyed grade, 300M.

The table below summarizes the main design properties requested for landing gears. MLX®19 has the best balance of properties: general corrosion, Ultra High Yield strength, damage tolerance, and stress corrosion cracking.

Brand names		MLX®17	MLX®19	Custom 465®	Ferrium® S53®	AISI 4340	AISI 300M	Aermet® 100	Ferrium® M54®
AMS standard		5937	5955	5936	5922	6414	6417	6532	6516
UTS	MPa ksi	1710 248	1895 275	1740 252	1985 288	1940 281	2000 290	2030 294	2020 293
YS0.2	MPa ksi	1620 235	1785 259	1690 245	1550 225	1670 242	1655 240	1710 248	1730 251
Elongation (%)		13	12	13	15	10	8.5	14	15
K_{IC}	MPa.√m ksi.√in	90 82	54 49	104 85	71 64	53 48	60 54	126 114	126 114
K_{ISCC}	MPa.√m ksi.√in	68 62	44 40	65 59	35 31	14 12	18 16	25 22	109 99
K_{ISCC}/K_{IC} (%)		75	80	60	50	25	30	20	86
General corrosion		High	High	High	Poor	No	No	No	No

Allowable design data is included in MMPDS-11.

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Ferrium® S53® and Ferrium® M54® are registered trademarks of Questek Innovations LLC

> APPLICATIONS IN DEFENSE

TECHNICAL CHALLENGES FOR MISSILE BODY AND FITTINGS

In the 60's, the large solid-propellant rocket motor program sparked the considerable research and development that has been conducted to take advantage of the properties of the 18%Ni maraging steels. These steels, combining high strength to weight ratio with good fracture toughness, ready weldability and simple heat treatment, became available just when such properties were needed to permit a scale-up in missile-case dimensions.

The 18%Ni maraging steels became the ideal choice for the fabrication of small rocket / missile cases and fittings designed for high performances:

- Ultra High Tensile Strength enables the material to withstand high pressure and the ability to manufacture light and thin-wall cases
- Weldability and the possibility to cold form enable a very simple manufacturing process

The precipitation hardening stainless steels bring today the same advantages in terms of manufacturing ability, availability and have been used for decades to offer corrosion resistance and stress corrosion cracking compared with 18%Ni maraging. The weak point until now was the lack of PH grades at an Ultra High Tensile Strength near 1900MPa.

MLX®19 BENEFITS

MLX®19 is very similar to 18%Ni maraging steels in term of:

- Ultra High Strength to weight ratio
- Availability in round bars, sheets, plates, forgings
- High weldability (GMAW, EBW, etc...)
- Cold forming ability and suitability for a specific process like flow-forming and extrusion

In addition, MLX®19 brings multiple advantages when compared to 18%Ni maraging steels:

- General corrosion resistance
- Stress corrosion cracking resistance
- Higher Young modulus (stiffness related design)

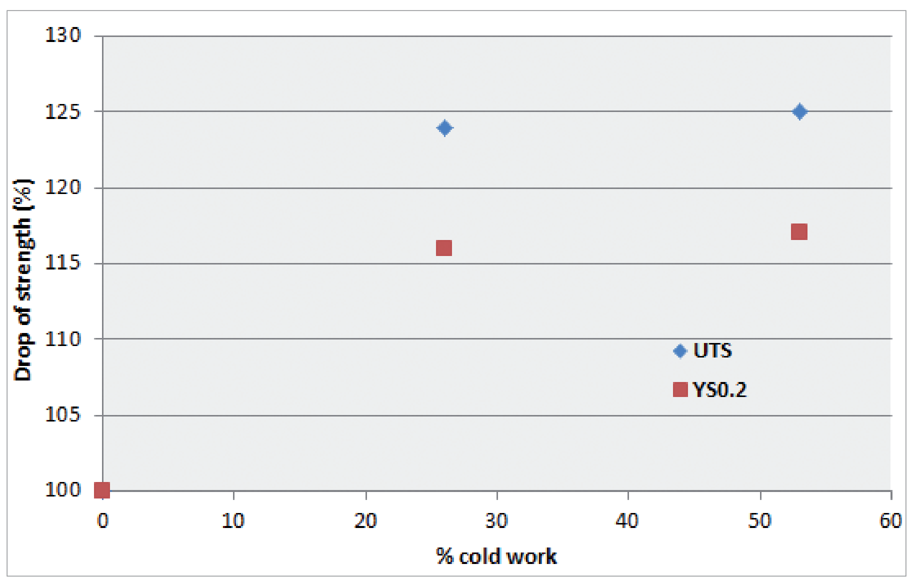
Brand names		Marval®X12H	MLX®17	MLX®19	Maraging250 Marval®18	Maraging300 MY19
AMS standard		5935	5937	5955	6512	6514
UTS	MPa ksi	1450 210	1710 248	1895 275	1792 260	2027 294
YS0.2	MPa ksi	1380 200	1620 235	1785 259	1758 255	1990 289
Elongation (%)		16	13	12	11	10
E modu-lus	GPa 10³ksi	193 27.9	193 27.9	195 28.3	182 26.4	182 26.4
K_{IC}	MPa.√m ksi.√in	140 127	90 82	54 49	100 91	65 59
K_{ISCC}	MPa.√m ksi.√in	120 109	68 62	44 40	18 16	13 11
General corrosion		High	High	High	No	No

COLD FORMING ABILITY

Because of a relatively low annealed yield strength and low work hardening rate, MLX®19 (as with the other Precipitation Hardened stainless grades) can be readily cold formed by drawing or rolling. Single step aging of cold worked material results in enhanced strengthening response as illustrated in the diagram.

After ageing, cold reduction applied in the solution treated condition leads to an increase of 17% on Ultimate Tensile Strength for an applied cold reduction ratio of about 25%.

The graph below illustrates the effect on mechanical properties of the percentage of cold work applied on sheets between solutioning at 850°C (1562°F) and ageing at 500°C (932°F) for 4 hours.



Properties measured in longitudinal direction, depending on applied cold work after annealing and before ageing

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FLOWFORMING ABILITY

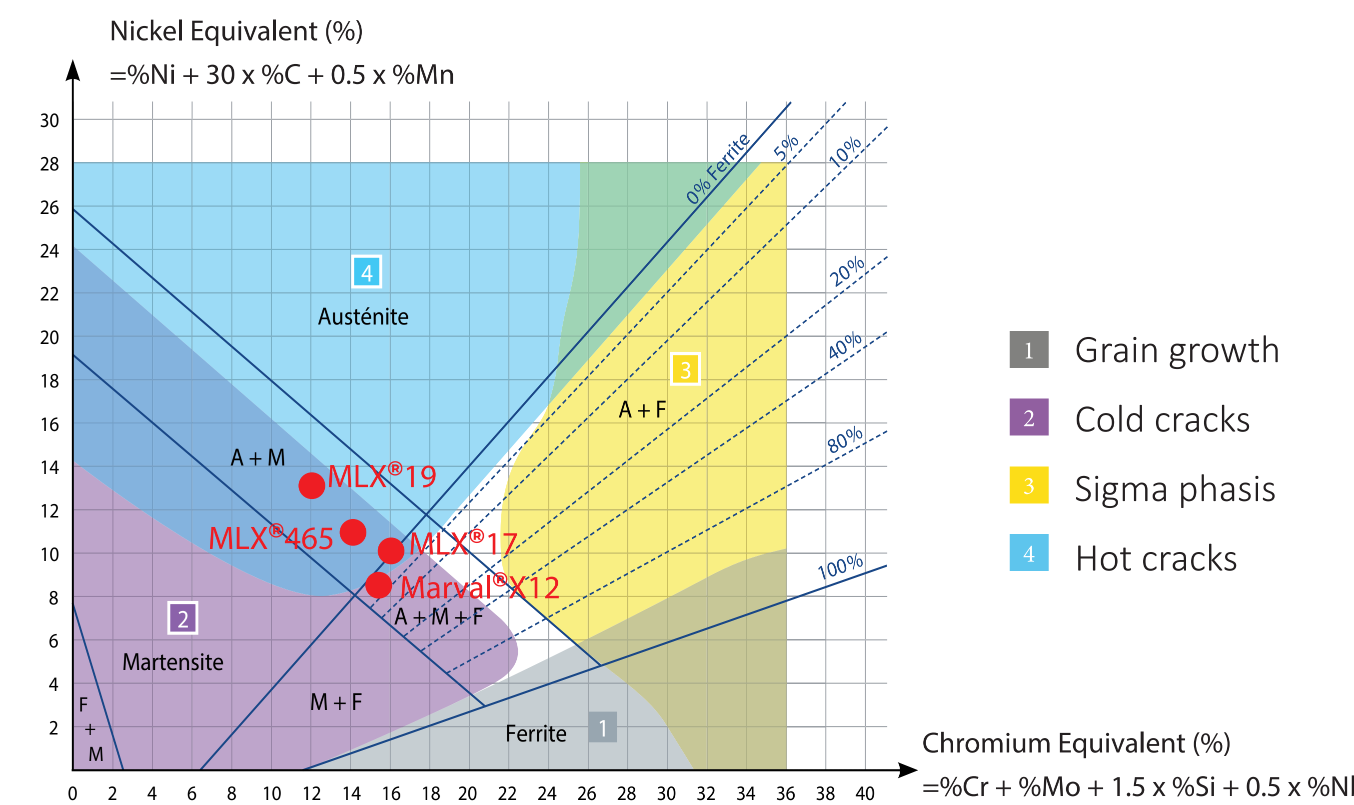
MLX®19, as with any other maraging and precipitation hardened stainless steels, is suitable for a flow forming process. This specific process targets achieving very thin wall sections with very accurate geometry and distorsion control. This process generates very high deformation ratios and leads to Ultra High Strength in the wall section (+15% UTS, +25% YS0.2). This must be applied in solution treated conditions; the ageing being done afterwards. Due to the low temperature ageing, distorsions can easily be managed.

WELDING ABILITY

MLX®19 can be successfully welded by the GTAW (Gas Tungsten Arc Welding) process using matching filler metal. According to the chemical composition and the solidification path, the main risk is the weld-bead hot cracking (behavior similar to Custom465® and less favorable than MLX®17). When the GMAW (Gas Metal Arc Welding) process is employed, MLX®19 filler metal is suggested to provide high strength. Welds should be fabricated employing the minimum amount of heat-input required to achieve complete penetration. If lower strength can be tolerated, Marval®X12 filler metal may be used.

Oxyacetylene welding is not recommended, since carbon pickup in the weld may occur. Preheating is not required to prevent cracking during the welding of this alloy.

The material has been welded satisfactorily in the solution annealed condition. Direct ageing of weldments on annealed base metal is possible, but hardness throughout the weld is not uniform and fatigue performances might be decreased. The optimum combination of properties is obtained by solution annealing and cold treating the weldment and then aging.



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> APPLICATIONS IN MOTORSPORT & CONSUMER GOODS

SHAFTS AND FASTENING SYSTEMS IN MOTORSPORT

The Motorsport market is continuously seeking weight savings and performance improvements. MLX®19 can be an excellent candidate for driveshafts desiring corrosion resistance. Static and fatigue performances of MLX®19 will perfectly match Maraging 250, widely used for chassis parts and driveshafts (including tripods), in motorsport (formula1, rallye or touring).

Brand names		MLX®19	AISI 300M	Maraging250
UTS	MPa ksi	1895 275	2000 290	1850 268
YS 0.2	MPa ksi	1785 259	1655 240	1780 258
Elongation (%)		12	12	10
E modulus	GPa 10^3ksi	195 28.3	199 28.9	182 26.4
K_{IC}	MPa.√m ksi.√in	54 49	60 54	100 91
Lf	MPa ksi	750 108	870 126	770 111
General corrosion		Yes	No	No

MLX®19 positively responds to stone chipping, enhancing fatigue performances. MLX®19 is also suitable for the nitriding process (gas or plasma). When a gas nitriding process is performed at 480°C (896°F) after ageing at 510°C (950°F), a nitrided case depth of about 0.2mm (0.008 inch) can be achieved with a top hardness surface higher than 1000HV (69HRC). A plasma nitriding process is compatible as well and can work under colder conditions.

For fastening systems, MLX®19 represents an attractive alternative to cold drawn MP35N® for structural applications. We recommend to perform threading after ageing, under medium temperature below 480°C (896°F).

MLX®19 cannot work longer than 10 000 hours at a temperature higher than 300°C (572°F) due to embrittlement and loss of corrosion performance linked with chromium rich alpha prime phase precipitation.

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AUBERT&DUVAL

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