

Crofer[®] 22 H

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High-temperature alloy

Crofer[®] 22 H

ThyssenKrupp VDM



ThyssenKrupp

Crofer® 22 H* is a high-temperature ferritic stainless steel especially developed for application in solid oxide fuel cells (SOFC). It has good creep strength because of Laves phase precipitates. At temperatures up to 900 °C (1652 °F) a chromium-manganese oxide layer is formed on the surface of Crofer® 22 H, which is thermodynamically very stable and possesses high electrical conductivity. The low coefficient of thermal expansion is matched to that of ceramics typically used for high temperature fuel cells in the range from room temperature to 900 °C (1652 °F).

Crofer® 22 H is characterized by:

- excellent corrosion resistance at high temperatures in anode gas and cathode gas
- good creep properties
- low rate of chromium vaporization
- ease of working and processing
- low coefficient of thermal expansion
- good electrical conductivity of the oxide layer

Designations and standards

Country	Material designation	Specification		
		Chemical composition	Sheet & Plate	Strip
National standards				
D	(W.-Nr. 1.4750)			
DIN EN	(X1CrWNbTiLa22)			
() Proposed new material designation				

Table 1 - Designations and standards.

Chemical composition

	Cr	Fe	C	N	S	Mn	Si	Al	W	Nb	Ti	La	P	Cu
min.	20.0	bal.				0.3	0.1		1.0	0.2	0.02	0.04		
max.	24.0		0.03	0.03	0.006	0.8	0.6	0.1	3.0	1.0	0.20	0.20	0.05	0.5

Table 2 – Chemical composition (wt.-%).

* ThyssenKrupp VDM GmbH produces Crofer® 22 H under license from Forschungszentrum Jülich.

Physical properties

Density	7.8 g/cm ³	0.278 lb/in. ³
Melting range	1452 °C (Solidus) - 1503 °C (Liquidus)	2646 °F (Solidus) - 2737 °F (Liquidus)

Temperature (T)		Electrical resistivity		Thermal conductivity		Specific heat		Coefficient of thermal expansion between 20 °C/68°F and T		Modulus of elasticity	
°C	°F	μΩ·cm	Ω·circ mil ft	$\frac{W}{m \cdot K}$	$\frac{Btu \cdot in.}{ft^2 \cdot h \cdot ^\circ F}$	$\frac{J}{kg \cdot K}$	$\frac{Btu}{lb \cdot ^\circ F}$	$\frac{10^{-6}}{K}$	$\frac{10^{-6}}{^\circ F}$	GPa	10 ³ ksi
20	68	56	337	20.0	139	469	0.112			208	30.2
100	212	65	391	20.6	143	494	0.118	9.8	5.5	207	30.0
200	392	74	445	21.5	149	532	0.127	10.1	5.7	203	29.3
300	572	82	493					10.5	5.8	196	28.4
400	752	89	535	22.6	157	615	0.147	10.8	6.0	190	27.6
500	932	96	577					11.0	6.1	182	26.4
600	1112	103	620	25.4	176	948	0.226	11.2	6.2	175	25.4
700	1292	107	644					11.4	6.3		
800	1472	109	656	26.1	181	660	0.158	11.8	6.6		
900	1652	111	668					12.3	6.8		
1000	1832	113	680	29.9	207	674	0.161	12.8	7.1		

Table 3 – Typical physical properties at room and elevated temperatures.

Mechanical properties

0.2 % Yield strength R _{p0.2}		Tensile strength R _m		Elongation A	Hardness HV
MPa	ksi	MPa	ksi	%	(For information only)
≥ 320	≥ 46.4	≥ 450	≥ 65.3	A ₅₀ ≥ 18* A ₅ ≥ 18** / A ₅ ≥ 8***	160 – 200

Thickness: * 0.2 – 2.5 mm (0.008 – 0.100”) / ** 3 - 16 mm (0.118 – 0.630”) / *** > 16 mm (0.630”)

Table 4 - Minimum mechanical properties in the soft-annealed condition for all product forms at room temperature.

Crofer[®] 22 H

Product	0.2 % Yield strength $R_{p0.2}$		Tensile strength R_m		Elongation A
	MPa	ksi	MPa	ksi	
Sheet & Plate 3 - 16 mm	370	53.7	500	72.5	22 (A_5)
> 16 mm	370	53.7	480	69.6	10 (A_5)
Strip	390	65.6	580	84.1	21 (A_{50})

Table 5 - Typical mechanical properties for different product forms at room temperature.

Temperature T		0.2 % Yield strength $R_{p0.2}$		Tensile strength R_m		Elongation A_5
°C	°F	MPa	ksi	MPa	ksi	
600	1112	160	23.2	333	48.3	28
700	1292	116	16.8	170	24.7	24
800	1472	54	7.8	85	12.3	65

Table 6 - Typical mechanical properties for plate (12 mm) at high temperatures.

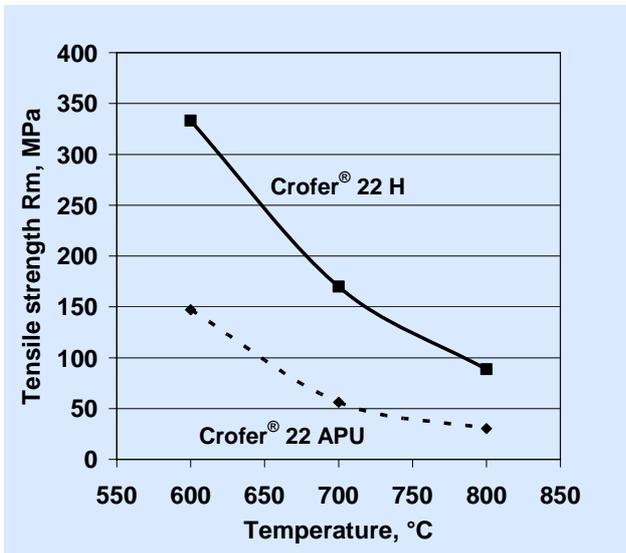


Fig. 1- Typical short-time mechanical properties Crofer[®] 22 H 12 mm plate as a function of temperature (solution annealed and about 2 hour at testing temperature before the test) in comparison to Crofer[®] 22 APU.

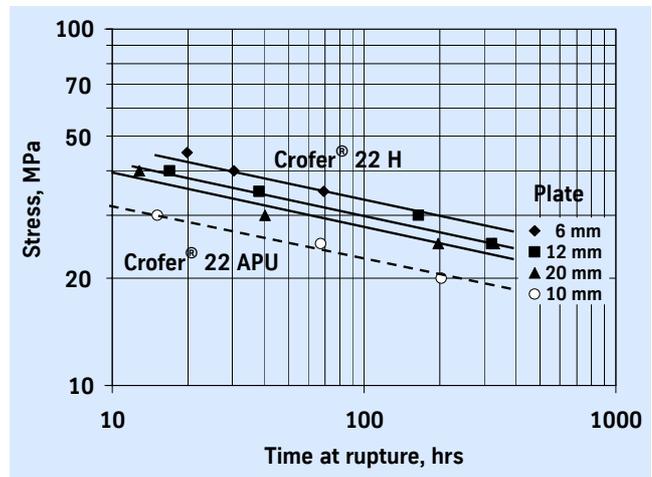


Fig. 2 – Typical stress-rupture tests of solution annealed Crofer[®] 22 H at 750 °C in air in comparison to Crofer[®] 22 APU.

Figure 1 shows that Crofer[®] 22 H clearly has a higher tensile strength than Crofer[®] 22 APU. Crofer[®] 22 H has also a markedly increased creep resistance as shown by stress-rupture tests in Figure 2. Time to rupture improves with decreasing plate thickness.

Metallurgical structure

Crofer[®] 22 H has a body-centered-cubic structure. During annealing at temperatures up to about 1000 °C (1832 °F) a Laves phase is formed which increases creep strength.

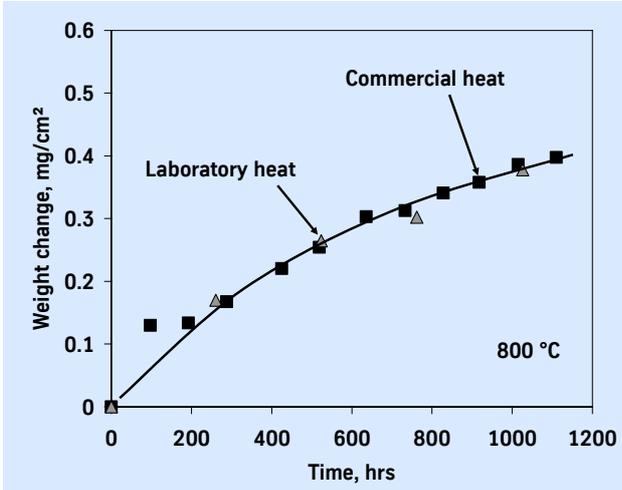


Fig. 3 - Mass change during discontinuous oxidation tests (100 h cycles) of a commercially produced Crofer® 22 H heat in air at 800 °C as a function of time. For comparison a laboratory melt (250 h cycles) is included (typical values). (After Quadackers, Niewolak et al., Forschungszentrum Jülich)

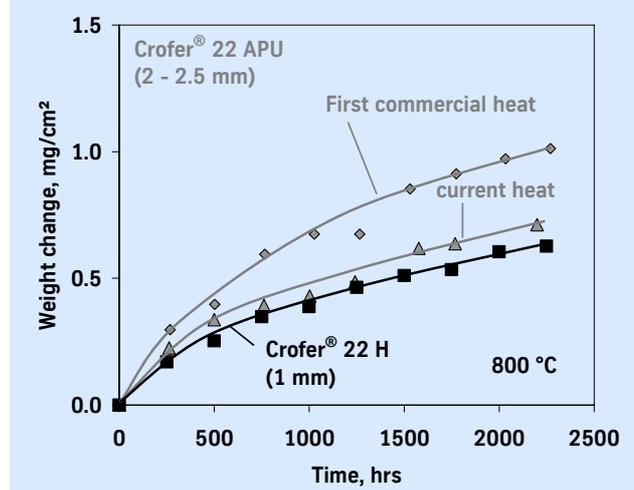


Fig. 5 - Mass change during discontinuous oxidation tests (250 h cycles) of commercially produced Crofer® 22 H and Crofer® 22 APU in air at 800 °C as a function of time. (typical values) (After Quadackers, Niewolak et al., Forschungszentrum Jülich)

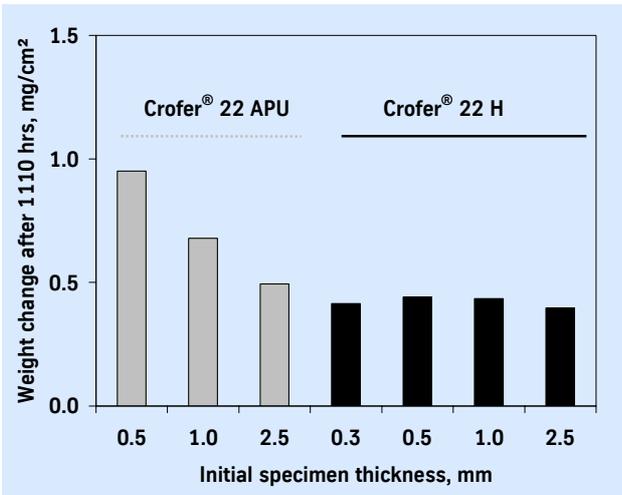


Fig. 4 - Mass change after 1110 hours of discontinuous oxidation tests (100 h cycles) in air at 800 °C of samples with varying thickness from Crofer® 22 H and Crofer® 22 APU (typical values). (After Quadackers, Niewolak et al., Forschungszentrum Jülich)

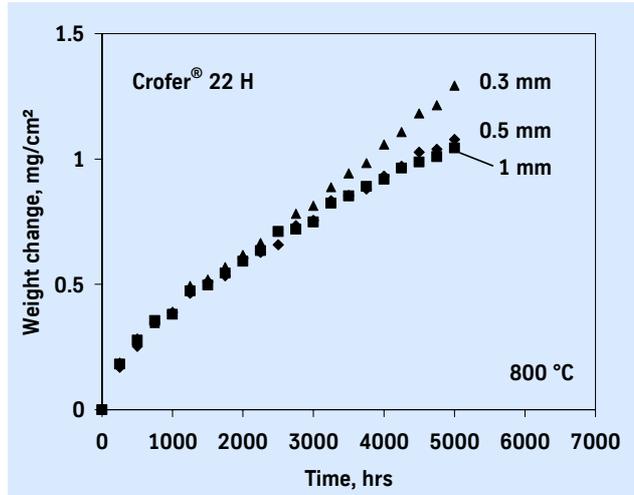


Fig. 6 - Mass change during discontinuous oxidation tests (250 h cycles) of commercially produced Crofer® 22 H in air at 800 °C as a function of time. (typical values) (After Quadackers, Niewolak et al., Forschungszentrum Jülich)

Corrosion resistance

Crofer® 22 H shows excellent corrosion resistance in atmospheres relevant to SOFC applications up to 900 °C. The oxide layer of Crofer® 22 APU consists of a fine grained inner scale which is predominantly Cr₂O₃ and a columnar (Mn, Cr)₃O₄ spinel outer oxide layer. Figure 3 shows the corrosion resistance of Crofer® 22 H in air at 800 °C for a commercial heat. For comparison the results of a laboratory heat melted with high-purity prematerials prior to the commercial heat are also included in Figure 3.

Figure 4 clearly shows that the thickness of sheet material has no significant effect on the corrosion resistance of Crofer® 22 H at 800 °C in air. On contrary there is a significant effect on the oxidation resistance of Crofer® 22 APU.

Figure 5 shows long term results of Crofer® 22 H and Crofer® 22 APU (first commercial melt and a heat from current production, which is restricted in residual

elements), which clearly shows the extraordinary good corrosion resistance of Crofer® 22 H.

Figure 6 shows long term results of Crofer® 22 H for different thicknesses. For 0.3 mm thickness after about 3000 hrs at 800 °C in air, corrosion increases in comparison to 0.5 mm and 1 mm thickness. For 0.5 mm and 1 mm thicknesses no influence of sheet thickness can be seen up to 5000 hrs.

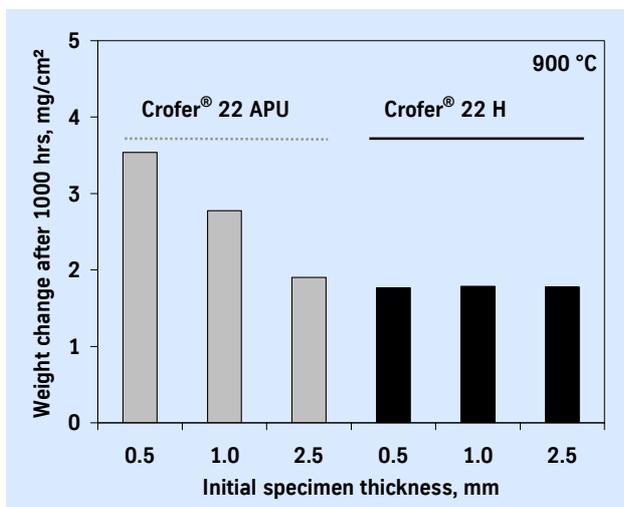


Fig. 7 - Mass change after 1000 hours of cyclic oxidation tests in air at 900 °C (cycles of 2 h and 15 min. cooling) of samples with varying thickness from commercially produced Crofer® 22 H and Crofer® 22 APU (typical values).
(After Quadakkers, Niewolak et al., Forschungszentrum Jülich)

Applications

Crofer® 22 H is used for interconnector plates to separate individual plates in solid oxide fuel cells (SOFC).

Fabrication and heat treatment

Crofer® 22 H can readily be hot and cold worked and machined.

Heating

Work pieces must be clean and free from all kinds of contaminants before and during any heating operations.

Crofer® 22 H may become embrittled if heated in the presence of contaminants such as sulfur, phosphorus, lead and other low-melting-point metals. Sources of such contaminants include marking and temperature-indicating paints and crayons, lubricating grease, fluids and fuels.

Figure 7 shows that the thickness of sheet material has also no significant effect on the corrosion resistance of Crofer® 22 H at 900 °C in air. On contrary there is a significant effect on the oxidation resistance of Crofer® 22 APU.

Figure 8 shows the corrosion resistance of Crofer® 22 H and Crofer® 22 APU at 800 °C in various gases, which again demonstrates the extraordinary good corrosion resistance of Crofer® 22 H.

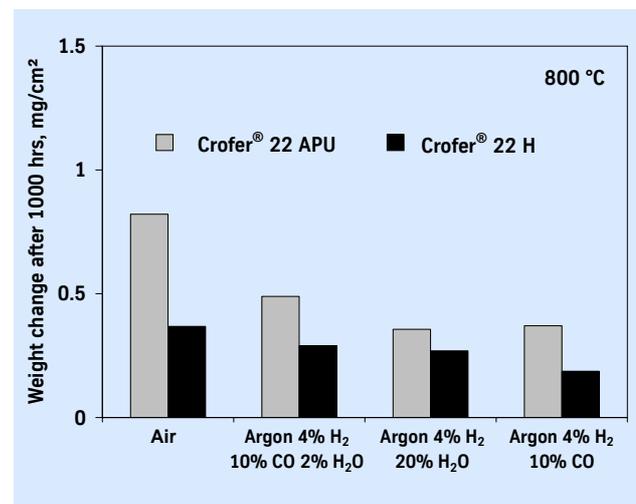


Fig. 8 - Mass change after 1000 hours of discontinuous oxidation tests (100 h cycles) in various gases at 800 °C of commercially produced Crofer® 22 H and Crofer® 22 APU for a sheet thickness of 1 mm (typical values).
(After Quadakkers, Niewolak et al., Forschungszentrum Jülich)

Fuels must be as low in sulfur as possible. Natural gas should contain less than 0.1 wt.-% sulfur. Fuel oils with a sulfur content not exceeding 0.5 wt.-% are suitable.

Due to their close control of temperature and freedom from contamination, thermal treatments in electric furnaces under vacuum or an inert gas atmosphere are to be preferred. Treatments in an air atmosphere and alternatively in gas-fired furnaces are acceptable though, if contaminants are at low levels so that a neutral or slightly oxidizing furnace atmosphere is attained.

A furnace atmosphere fluctuating between oxidizing and reducing must be avoided as well as direct flame impingement on the metal.

Cold working

For cold working the solution annealed condition is recommended.

Heat treatment

A solution annealing can be performed at temperatures typically above 1050°C, followed by a quenching in water.

After cold forming a recrystallization thermal treatment (soft annealing), typically above 1050 °C, is required.

Descaling and pickling

Oxides of Crofer[®] 22 H and discoloration adjacent to welds are more adherent than on standard stainless steels. Grinding with very fine abrasive belts or discs is recommended. Care should be taken to prevent tarnishing.

Before pickling which may be performed in a nitric/hydrofluoric acid mixture the surface oxide layer must be broken up by abrasive blasting, by carefully performed grinding or by pretreatment in a fused salt bath. Particular attention should be paid to the pickling time and temperature.

Welding

When welding nickel alloys and high alloyed stainless steels, the following instructions should be adhered to:

Workplace

The workplace should be in a separate location, well away from areas where carbon steel fabrication takes place. Maximum cleanliness and avoidance of draughts are paramount.

Auxiliaries, clothing

Clean fine leather gloves and clean working clothes should be used.

Tools and machines

Tools used for nickel alloys and high alloyed stainless steels must not be used for other materials. Brushes should be made of stainless materials.

Fabricating and working machinery such as shears, presses or rollers should be fitted with means (felt, cardboard, plastic sheeting) of avoiding contamination of the metal with ferrous particles, which can be pressed into the surface and thus lead to corrosion.

Cleaning

Cleaning of the base metal in the weld area (both sides) and of the filler metal (e.g. welding rod) should be carried out with ACETONE.

Trichlorethylene (TRI), perchlorethylene (PER), and carbon tetrachloride (TETRA) must not be used as they are detrimental to health.

Edge preparation

This should preferably be done by mechanical means by turning, milling or planing; abrasive water jet or plasma cutting is also suitable. However, in the latter case the cut edge (the face to be welded) must be finished off cleanly. Careful grinding without overheating is permitted.

Striking the arc

The arc should only be struck in the weld area, i.e., on the faces to be welded or on a run-out piece. Striking marks lead to corrosion.

Welding process

Crofer[®] 22 H in thin thicknesses (≤ 1.5 mm/0.06 in.) can be joined to itself by GTAW (TIG) without the use of filler metal. It can also be joined by spot welding or roll-seam welding.

For welding, Crofer[®] 22 H should be in the soft-annealed condition and be free from scale, grease and markings. Argon 4.8 is recommended for shielding gas as well as for root backing. A hydrogen and/or nitrogen containing gas should be avoided. Any heat tint should be removed preferably by brushing with a stainless steel wire brush while the weld metal is still hot.

Welding parameters and influences (heat input)

Care should be taken that the work is performed with a deliberately chosen, low heat input. The heat input per unit length should not exceed 8 kJ/cm.

Postweld treatment

(brushing, pickling and thermal treatments)

Brushing with a stainless steel wire brush immediately after welding, i.e., while the metal is still hot, generally results in removal of heat tint and produces the desired surface condition without additional pickling.

For pickling refer to the information under “**Descaling and pickling**”

Neither pre- nor postweld thermal treatments are normally required.

Availability

Crofer[®] 22 H is available as sheet & plate and strip.

Sheet & Plate

(for cut-to-length availability, refer to strip)

Conditions

hot or cold rolled (hr, cr), soft annealed and pickled

Thickness mm	hr/cr	Width ¹⁾ mm	Length ¹⁾ mm
1.10 - < 1.50	cr	2000	8000
1.50 - < 3.00	cr	2500	8000
3.00 - < 7.50	cr/hr	2500	8000
7.50 - ≤ 25.00	hr	2500	8000 ²⁾
> 25.00 ¹⁾	hr	2500 ²⁾	8000 ²⁾

¹⁾ Other sizes subject to special enquiry²⁾ Depending on piece weight

Thickness inches	hr/cr	Width ¹⁾ inches	Length ¹⁾ inches
0.043 - < 0.060	cr	80	320
0.060 - < 0.120	cr	100	320
0.120 - < 0.300	cr/hr	100	320
0.300 - ≤ 1.000	hr	100	320 ²⁾
> 1.000 ¹⁾	hr	100 ²⁾	320 ²⁾

¹⁾ Other sizes subject to special enquiry²⁾ Depending on piece weight**Strip¹⁾****Conditions**cold rolled, soft annealed and pickled or bright annealed²⁾

Thickness mm	Width ³⁾ mm	Coil I.D. mm
0.02 - ≤ 0.10	4 - 200 ⁴⁾	300 400
> 0.10 - ≤ 0.20	4 - 350 ⁴⁾	300 400 500
> 0.20 - ≤ 0.25	4 - 750	400 500 600
> 0.25 - ≤ 0.60	6 - 750	400 500 600
> 0.60 - ≤ 1.0	8 - 750	400 500 600
> 1.0 - ≤ 2.0	15 - 750	400 500 600
> 2.0 - ≤ 3.0 ²⁾ - ≤ 3.5 ²⁾	25 - 750	400 500 600

¹⁾ Cut-to-length available in lengths from 250 to 4000 mm²⁾ Maximum thickness: bright annealed - 3 mm
cold rolled only - 3.5 mm³⁾ Wider widths subject to special enquiry⁴⁾ Wider widths up to 730 mm subject to special enquiry

Thickness inches	Width ³⁾ inches	Coil I.D. inches
0.0008 - ≤ 0.004	0.16 - 8 ⁴⁾	12 16
> 0.004 - ≤ 0.008	0.16 - 14 ⁴⁾	12 16 20
> 0.008 - ≤ 0.010	0.16 - 30	16 20 24
> 0.010 - ≤ 0.024	0.24 - 30	16 20 24
> 0.024 - ≤ 0.040	0.32 - 30	16 20 24
> 0.040 - ≤ 0.080	0.60 - 30	16 20 24
> 0.080 - ≤ 0.120 ²⁾ - ≤ 0.140 ²⁾	1.00 - 30	16 20 24

¹⁾ Cut-to-length available in lengths from 10 to 158 in.²⁾ Maximum thickness: bright annealed - 0.120 in.
cold rolled only - 0.140 in.³⁾ Wider widths subject to special enquiry⁴⁾ Wider widths up to 29 in. subject to special enquiry

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ThyssenKrupp VDM GmbH

Plettenberger Strasse 2

58791 Werdohl

P.O. Box 1820

58778 Werdohl

Germany

Phone: +49 2392 55-0

Fax: +49 2392 55-2217

Email: vdm@thyssenkrupp.comwww.thyssenkruppvdm.com