Crofer 22 APU

Material Data Sheet No. 4046
June 2008 Edition

High-temperature alloy

A company of
ThyssenKrupp
Stainless

ThyssenKrupp VDM

ThyssenKrupp

Crofer 22 APU*

Crofer 22 APU* is a high-temperature ferritic stainless steel especially developed for application in solid oxide fuel cells (SOFC).

At temperatures up to 900 °C (1652 °F) a chromium-manganese oxide layer is formed on the surface of Crofer 22 APU 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 APU is characterized by:

- excellent corrosion resistance at high temperatures in anode gas and cathode gas
- 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 National standard	Material designation	Spezification			
		Chemical composition	Sheet & Plate	Strip	Wire
D DIN EN	**W.-Nr. 1.4760** X1CrTiLa22				
USA ASTM	UNS S44535	A 240	A 240		

Table 1 - Designations and standards.

Chemical composition

	Cr	Fe	C	Mn	Si	Cu	Al	S	P	Ti	La
min.	20.0	bal.		0.30						0.03	0.04
max.	24.0		0.03	0.80	0.50	0.50	0.50	0.020	0.050	0.20	0.20

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

* *ThyssenKrupp VDM GmbH produces Crofer 22 APU (APU = Auxiliary Power Unit) under licence from Forschungszentrum (FZ) Jülich.*

Physical properties

Density	7.7 g/cm³	0.278 lb/in.³
Melting temperature	1510 (Solidus) - 1530 °C (Liquidus)	2750 (Solidus) - 2786 °F (Liquidus)

Temperature (T)		Specific heat		Thermal conductivity		Electrical resistivity		Modulus of elasticity		Coefficient of thermal expansion between 20 °C/68 °F and T	
°C	°F	J/(kg · K)	Btu/(lb · °F)	W/(m · K)	Btu · in./(ft² · h · °F)	μΩ · cm	Ω · circ mil/ft	kN/mm²	10³ ksi	10⁻⁶/K	10⁻⁶/°F
25	77	470	0.112	26	180	55	330	220	31.9		
200	392	520	0.124	23	160	70	421	210	30.5	10.3	5.7
400	752	610	0.146	23	160	90	541	195	28.3	10.8	6.0
500	932							183	26.5	11.2	6.2
600	1112					105	632			11.4	6.3
700	1292									11.6	6.4
800	1472	660	0.158	24	166	115	692			11.9	6.6
900	1652									12.3	6.8
1000	1832	650	0.155	27	187	120	722			12.7	7.1

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

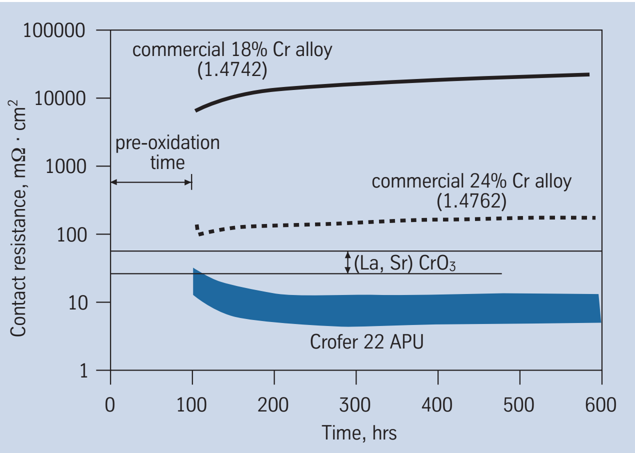

Fig. 1 – Contact resistance of various materials used for SOFC in air at 800 °C (typical values). (After Quadakkers et al., FZ Jülich)

Figure 1 shows the contact resistance of Crofer 22 APU as a function of time while exposed to air at 800 °C. The contact resistance of Crofer 22 APU is an order of magnitude lower than traditional ferritic alloy 446 (1.4762) type stainless steels. This is because Crofer 22 APU forms a protective scale that exhibits good electrical conductivity and no SiO_2 sublayer which shows poor electrical conductivity.

Crofer 22 APU

Mechanical properties

0.2% Yield strength $R_{p\,0.2}$		Tensile strength R_m		Elongation A_{50}	Hardness HRB
MPa	ksi	MPa	ksi	%	(For information only)
≥ 250	≥ 36.6	≥ 350	≥ 50.8	≥ 20* / ≥ 25**	70 – 90
Thickness: *0.25 – 0.38 mm (0.010 – 0.015”) / ** ≥ 0.38 mm (0.015”)					

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

Product	0.2% Yield strength $R_{p\,0.2}$		Tensile strength R_m		Elongation A_{50}
	MPa	ksi	MPa	ksi	%
Sheet & Plate	270	39.1	370	53.7	30
Strip	320	46.4	450	65.3	30
Wire	350	50.8	500	72.5	15

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

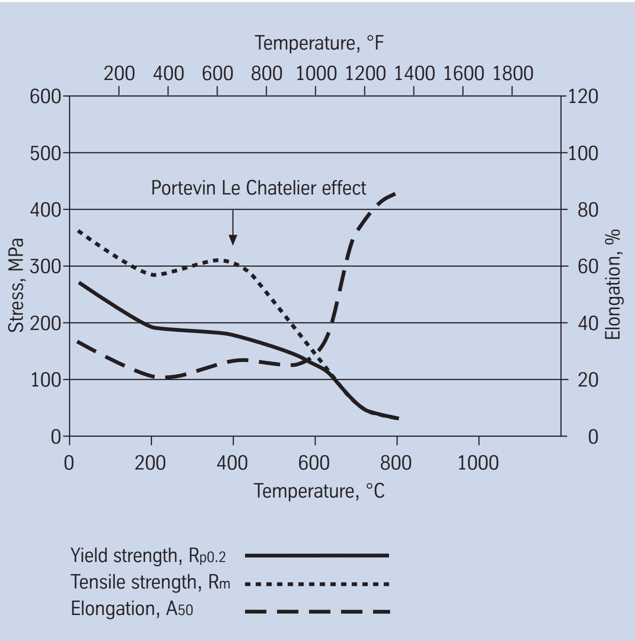

Fig. 2 - Typical short-time mechanical properties of soft annealed Crofer 22 APU 22 mm plate as a function of temperature.

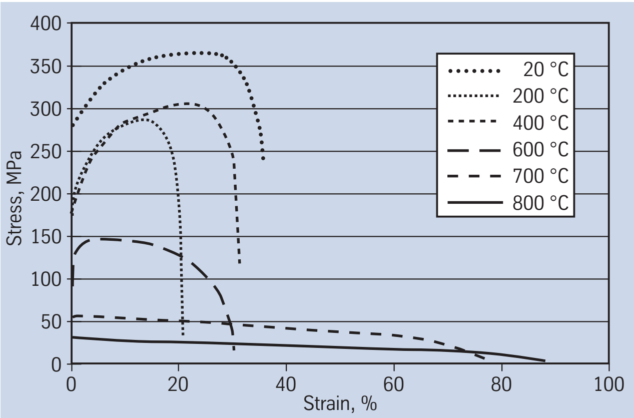

Fig. 3 - Typical Stress-Strain Curves for Crofer 22 APU at various temperatures.

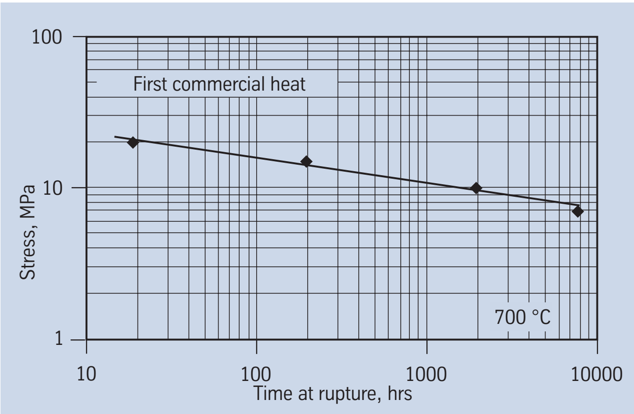

Fig. 4 - Typical Creep-rupture strength of soft annealed Crofer 22 APU from the first commercial heat at 700 °C in air.

Corrosion resistance

Crofer 22 APU 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 Cr_2O_3 and a columnar $(Mn, Cr)_3O_4$ spinel outer oxide layer.

This outer layer reduces chromia evaporation very effectively as shown in Figure 5.

Figures 6 to 9 show the corrosion resistance of Crofer 22 APU in atmospheres relevant to SOFC applications at 800 °C and 900 °C respectively.

Current production restricts the residual element content in comparison to the first commercial heat. This results in a vast improvement of the oxidation behavior as clearly shown in Figures 6 to 9 for several commercial heats (sample thickness ranging from 1.5 to 2 mm). For comparison the results of the laboratory heat melted with high-purity prematerials prior to the first commercial heat are also included in Figures 6, 8 and 9.

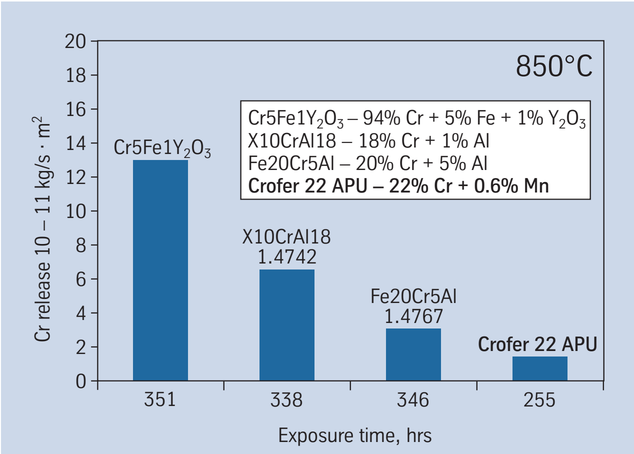

Fig. 5 - Chromium release of several materials at 850 °C in humidified synthetic air with 2% H_2O (2 x 10^3 Pa) (typical values). (After Hilpert, Gindorf et al., Forschungszentrum Jülich)

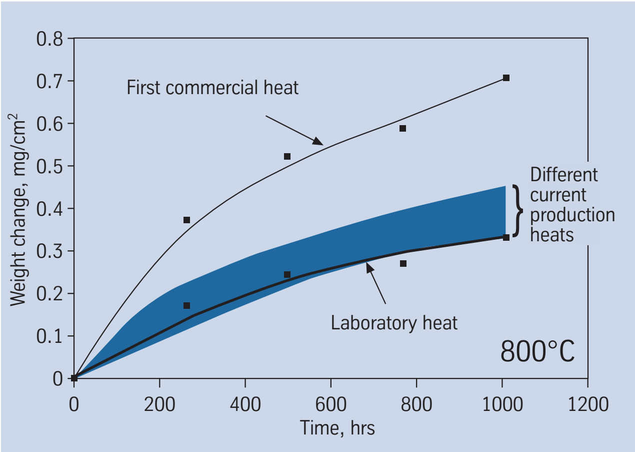

Fig. 6 - Mass change during discontinuous oxidation tests (250 h cycles) of a laboratory and commercially produced Crofer 22 APU heats in air at 800 °C as a function of time (typical values). (After Quadakkers et al., Forschungszentrum Jülich)

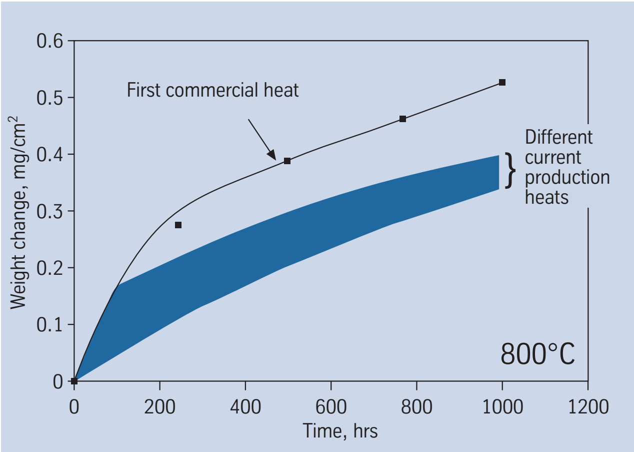

Fig. 7 - Mass change during discontinuous oxidation tests (100 h cycles except for the first commercial heat, where 250 h cycles were used) of commercially produced Crofer 22 APU heats in simulated anode gas (Ar + 4% H_2 + 2% H_2O) at 800 °C as a function of time (typical values). (After Quadakkers et al., Forschungszentrum Jülich)

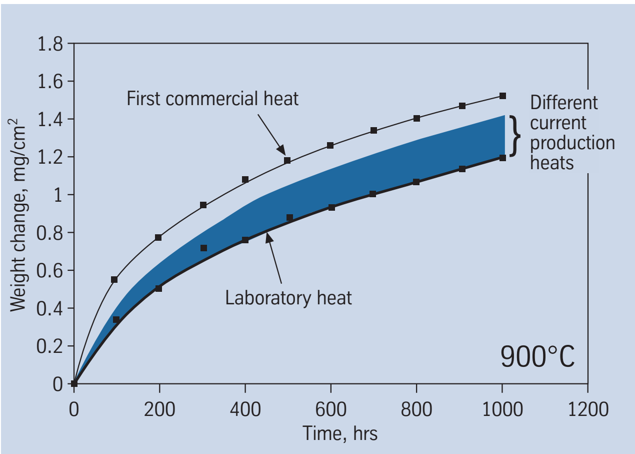

Fig. 8 - Mass change during discontinuous oxidation tests (100 h cycles) of a laboratory and commercially produced Crofer 22 APU heats in simulated anode gas (Ar + 4% H_2 + 20% H_2O) at 900 °C as a function of time (typical values) (After Quadakkers et al., Forschungszentrum Jülich)

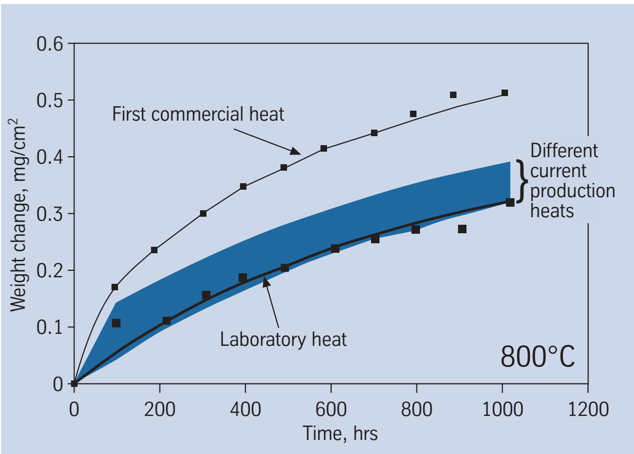

Fig. 9 - Mass change during discontinuous oxidation tests (100 h cycles) of a laboratory and commercially produced Crofer 22 APU heats in simulated carbon containing anode gas (Ar + 4% H_2 + 10% CO + 2% H_2O) at 800 °C as a function of time (typical values). (After Quadakkers et al., FZ Jülich)

Crofer 22 APU

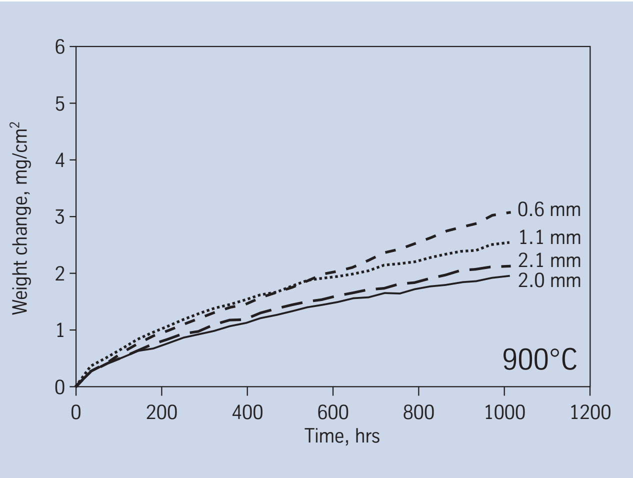

Fig. 10 - Mass change during cyclic oxidation tests in air (cycles of 2 h heating and 15 min. cooling) of samples of varying thickness from a Crofer 22 APU production heat restricted in residual elements (typical values). (After Quadakkers et al., Forschungszentrum Jülich)

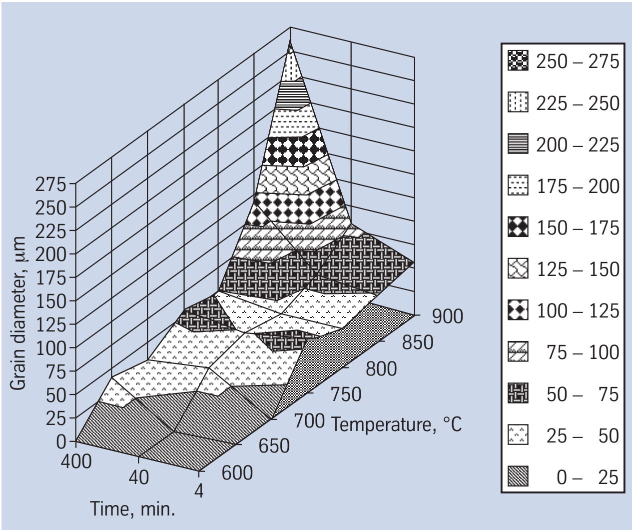

Fig. 11 - Typical Recrystallization diagram of Crofer 22 APU after 50% cold deformation.

Apart from the restriction in residual elements Figure 10 clearly shows that the thickness of sheet material also has a significant effect on the oxidation resistance of Crofer 22 APU.

Applications
Crofer 22 APU is used for interconnector plates to seperate individual plates in solid oxide fuel cells (SOFC).

Fabrication and heat treament
Crofer 22 APU can readily be hot and cold worked and machined.

Heat treatment
Workpieces must be clean and free from all kinds of contaminants before and during any heating operations.

Crofer 22 APU 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.

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.

After cold forming a recrystallization thermal treatment is required. Fig. 11 shows the effect on grain size of 50 % cold formed Crofer 22 APU of such a thermal treatment for various temperatures and time-at-temperature intervals.

Descaling and pickling
Oxides of Crofer 22 APU 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 in a nitric/hydroflouric acid mixture, the surface oxide layer must be broken up by abrasive blasting or 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, 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 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.

Included angle
The different physical characteristics of nickel alloys and special stainless steels compared with carbon steel generally manifest themselves in a lower thermal conductivity and a higher rate of thermal expansion.

This should be allowed for by means of, among other things, wider root gaps or openings (2 mm ≤ 0.5 mm), while larger included angles (60 – 70°), as shown in Fig. 12, should be used for individual butt joints owing to the viscous nature of the molten weld metal and to counteract the pronounced shrinkage tendency.

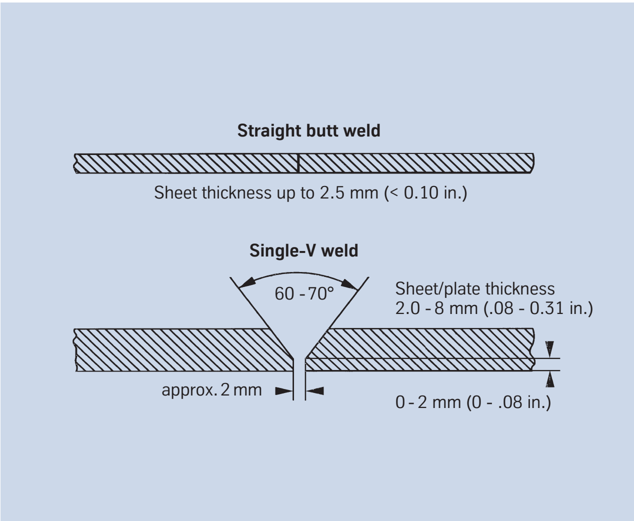

Fig. 12 – Edge preparation for welding of Crofer 22 APU.

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 APU in thin thicknesses (≤ 1.5 mm/0.06 in.) can be joined to itself by GTAW (TIG) and plasma arc welding without the use of filler metal. It can also be joined by spot welding or roll-seam welding.

For welding, Crofer 22 APU should be in the soft-annealed condition and be free from scale, grease and markings. When welding the root, care should be taken to achieve best-quality root backing (argon 99.99), so that the weld is free from oxides after welding the root. Any heat tint should be removed preferably by brushing with a stainless steel wire brush while the weld metal is still hot.

Filler metal
For the GTAW (TIG) welding process filler metal with the same composition as the base metal is recommended.

Welding parameters and influences (heat input)
Care should be taken that the work is performed with a deliberately chosen, low heat input as indicated in Tables 6 and 7 by way of example. Use of the stringer bead technique should be aimed at. Interpass temperature should be kept below 120 °C (250 °F).

The welding parameters should be monitored as a matter of principle.

The heat input Q may be calculated as follows:

$$Q = \frac{U \times I \times 60}{v \times 1000} \text{ (kJ/cm)}$$

U = arc voltage, volts
I = welding current, amps
v = welding speed, cm/min.

Consultation with ThyssenKrupp VDM’s Welding Laboratory is recommended.

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.

Pickling, if required or prescribed, however, would generally be the last operation performed on the weldment. Also refer to the information under **‘Descaling and pickling’**.

Neither pre- nor postweld thermal treatments are normally required.

Sheet/ plate thick-ness mm	Welding-process	Filler metal diameter mm	Filler metal speed m/min.	Welding parameters Root pass I A	Root pass U V	Intermediate and final passes I A	Intermediate and final passes U V	Welding speed cm/min.	Shielding gas Type & rate l/min.	Plasma gas Type & rate l/min.
3.0	Manual GTAW	2.0		80	10	110 – 120	11	approx. 15	Ar 4.6 8 – 10	
5.0	Manual GTAW	2.0 – 2.4		90 – 100	11	130 – 140	13	14 – 16	Ar 4.6 8 – 10	
3.0	Autom. GTAW	1.2	approx. 1.2	Manual GTAW		160	11	25	Ar 4.6 12 – 14	
5.0	Autom. GTAW	1.2	approx. 1.4	Manual GTAW		200 – 220	approx. 13	25	Ar 4.6 12 – 14	
3.0	Hot wire GTAW	1.0				180	11	80	Ar 4.6 12 – 14	
5.0	Hot wire GTAW	1.2		Manual GTAW		220	13	40	Ar 4.6 12 – 14	
4.0	Plasma arc	1.2	approx. 1.0	approx. 180	25			30	Ar 4.6 30	Ar 4.6 3.0
6.0	Plasma arc	1.2	approx. 1.0	200 – 220	26			26	Ar 4.6 30	Ar 4.6 3.5
In all gas-shielded welding operations, adequate back shielding using Ar 4.6 must be ensured. Figures are for guidance only and are intended to facilitate setting of the welding machines.										

Table 6 – Welding parameters (guide values).

Welding process	Heat input per unit length kJ/cm
GTAW, manual, fully mechanised	max. 8
Hot wire GTAW	max. 6
Plasma arc	max. 10

Table 7 – Heat input per unit length (guide values).

Technical Publications

The following publications concerning Crofer 22 APU may be obtained from ThyssenKrupp VDM GmbH or can be downloaded from www.thyssenkruppvdm.com:

R. Hojda, W. Heimann, W.J. Quadakkers:
Production - capable materials concept for high-temperature fuel cells; ThyssenKrupp techforum, July 2003.

R. Hojda:
Großserientaugliches Werkstoffkonzept für Brennstoffzellen; SCOPE - Das moderne Industriemagazin, April 2004.

R. Hojda, W. J. Quadakkers:
Improved product Crofer 22 APU; Reprint RP 1/05 from ThyssenKrupp techforum, July 2005.

R. Hojda, L. Paul:
UNS S44535 alloy development for interconnect applications in solid oxide fuel cells; CORROSION 2006, Paper No. 06479, NACE International, Houston, 2006.

H. Hattendorf:
Sulfur Tolerant Anode Material for Solid Oxide Fuel Cells; 2007 Fuel Cell Seminar; San Antonio, Texas, October 2007.

Further publications concerning Crofer 22 APU and solid oxide fuel cells (SOFC) may be obtained from the Forschungszentrum Jülich, Dept. IEF-2, 52425 Jülich, Germany.

Availability

Crofer 22 APU is available as sheet & plate, strip, and wire.

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

[1] Other sizes subject to special enquiry

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

[1] Other sizes subject to special enquiry

Strip[1]

Conditions:
cold rolled, soft annealed and pickled or bright annealed[2]

Thickness mm	Width[3] mm	Coil I.D. mm
0.02 - ≤ 0.10	4 - 200[4]	300 400
> 0.10 - ≤ 0.25	4 - 720[4]	300 400 500
> 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 mm
[2] Maximum thickness: bright annealed - 3 mm
cold rolled only - 3.5 mm
[3] Wider widths subject to special enquiry
[4] 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 - ≤ 0.010	0.16 - 14[4]	12 16 20
> 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 enquiry
[4] Wider widths up to 29 in. subject to special enquiry

Wire

Conditions:
drawn, bright, thermally treated;
drawn, bright, thermally treated, redrawn ¼ hard to hard;
shaved or ground.

Dimensions:
drawn wire: 0.16 – 10 mm (0.0063 – 0.40 in.) diameter,
on spools, in coils and payoff packs; also available on spiders and special spools.

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