

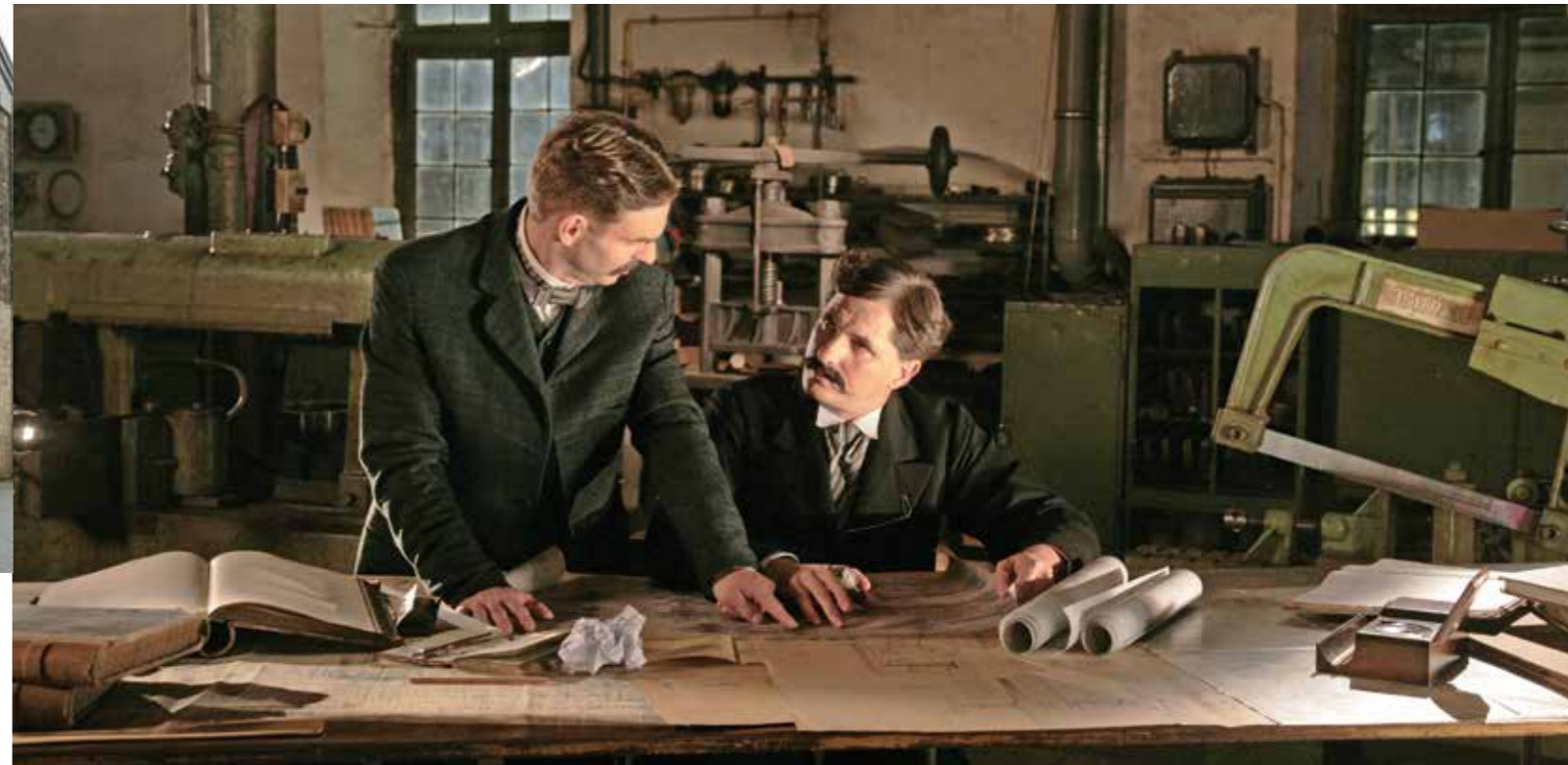


High-alloy Materials for Boiler Tubes



MANNESMANN
STAINLESS TUBES

A Member of the Salzgitter Group



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Seamless stainless steel and nickel-based alloy tubes and pipes are our everyday passion and our history at Mannesmann Stainless Tubes. As early as 1885 Reinhard and Max Mannesmann invented a rolling process for the production of seamless steel tubes in Remscheid, Germany. In the 1890's they developed it further until it reached marketability: the production method they invented was the pilger process, which still is widely in use today.

Our group integrates the tradition of three seamless stainless steel worlds (Mannesmann, Dalmine and Vallourec). Resulting in "DMV Stainless" from this international merger in 1994, DMV became a part of Salzgitter group in 2003 and adjusted its name to Salzgitter Mannesmann Stainless Tubes in 2008.

With an international network of plants and offices, we are a global top player in our markets and a consistently reliable business partner, ensuring quick and customer focused answers to changing market requirements.

Our customers profit from one of the most comprehensive product ranges in our business:

- from small instrumentation tubing to large pipe sizes with outside diameters from 6 to 250 mm (from 0.24 up to 9.84 inches) and with wall thicknesses from 0.5 up to 50 mm (from 0.02 up to 1.97 inches)

- in materials from standard austenitic stainless, duplex and super-duplex steels to highly sophisticated nickel-based alloys – this variety offers highest corrosion resistance, heat resistance and/or high-temperature, high-strength materials.

We combine high quality products for critical environments with efficient and reliable services: our customers thus enjoy a supportive personal account management.

Ongoing cycles of investment ensure that we work according to the latest technical standards. This gives us the trustworthiness to equip the so called "critical spots" of customers' plants, products and processes with the special qualities of our tubes and pipes.

Typically, these "critical" service conditions are defined e.g. by

- high temperatures
- high pressure
- aggressive media (acids or basic)

Basic material challenges

Operating conditions within newly constructed power stations are critically determined by recent developments in boiler fabrication. The use of heat resistant high-alloy steels in this construction allows the determination of reliably improved supercritical steam characteristics.

These alloys, not only improve plant efficiency, they also allow reduced volumes of materials, both of which translate into positive economic benefits. Moreover, the more acute the environmental conditions imposed upon combustion emissions, the more effective and economic these materials become. Outstanding hot strength properties of heat resistant austenitic steels and nickel base alloys make their use excellent for resistance to hot gases. Operational temperatures for this group of materials start above 550°C. Their suitability for pressure vessel fabrication may be verified by reviewing their material design characteristics and the long-term strength values that have been determined through creep tests made over periods of up to 200,000 hours.

The hot strength properties of our boiler tubing materials make them suitable for use in pressure-bearing plants having operating temperatures of up to 1,000°C. They also have excellent fabrication characteristics necessary for tube materials used in high temperature boiler plant construction.

MST designation	Germany		USA		France		Great Britain		Japan	
	W-Nr	DIN	UNS	ASTM	Designation	NFA	Designation	BS	Designation	JIS
DMV 304 H	1.4948	17459	S30409	A 376 ¹⁾	Z 6 CN 19-10	49-214	304 S 51	3059	304 HTP	3459
DMV 304 HCu	1.4907		Code Case 2328-1							
DMV 304 N	1.4949	17459	S30451	A 376 ¹⁾			304 S 51	3059		
DMV 316 H	1.4919	17459	S31609	A 376 ¹⁾	Z 6 CN 17-12B	49-214	316 S 52	3059	316 HTP	3459
DMV 321 H	1.4941	17459	S32109	A 376 ¹⁾	Z 6 CN 18-12B	49-214	321 S 51	3059	321 HTP	3459
DMV 347 H	1.4550	17458	S34700	A 376 ¹⁾	Z 6 CNb 18-10	49-218	347 S 59	3059	347 HTP	3459
DMV 347 HFG	1.4908		Code Case 2159-2							
DMV 4910	1.4910	17459	S31653	A 376 ¹⁾	Z 6 CN 19-10	49-214	316 S 51	3059		
DMV 310 N	1.4952		S31042	A 213						
DMV 800 H	1.4958	17459	N08810	B 407	Z 8 NC 32-21	35-578	NA 15	3074	NOF800 H	
DMV 800 HT	1.4959	17459	N08811	B 407	Z 8 NC 32-21	35-578	NA 15	3074	NOF800 H	
DMV AC 66	1.4877		S33228	A 213						
DMV 600 H	2.4816	17751	N06600	B 167	Z 8 NC 75 15		NA 14(H)3074	3074	NOF600H	
DMV 617 / DMV 617 mod.	2.4663		N06617	B 622						

Table 1: Equivalent grades according to national and international standards

Characterization of heat resistant materials

Table 1 lists the international designations for selected MST materials having improved austenite stability. The stability of the austenite in CrNi and CrNiMo steels is achieved by increasing the nickel content over that of standard 18/8 CrNi and 18/8/2 CrNiMo steels, and more especially by additions of nitrogen, which is particularly effective in promoting the austenite stability.

Typical properties of austenitic heat resistant materials include:

- high creep rupture strength above 550 °C
- outstanding resistance to high-temperature corrosion and oxidation
- excellent processing characteristics.

¹⁾ also ASTM A 213, ASTM A 312, ASME

Creep rupture strength

Excellent creep rupture strength is one of the most important properties of materials used in pressure vessel construction and power station engineering. Table 4 lists the specified creep rupture strength values for MST materials.

These differences can be attributed to metallurgical changes related to specific alloying. The stainless steel alloys with the highest creep rupture strength are the “supercritical” grades DMV 304 HCu, DMV 347 HFG and DMV 310 N.

The high creep rupture strength of DMV 304 HCu is due to the strengthening effect of fine Cu-rich precipitates in the austenite matrix, which are formed during service in the temperature range between 580 °C and 640 °C (1,075 and 1,185 °F).

The increase in creep rupture strength in the high-nickel steels DMV 800 H , DMV 800 HT and DMV AC 66 is due to precipitates in the matrix. The high creep rupture strength of nickel base alloys is either achieved by precipitation hardening (e.g. DMV 600 H) or by solid-solution hardening (DMV 617 mod.).

Among the materials in table 2, are the high-nickel steels DMV AC 66, DMV 800 H, DMV 800 HT as well as nickel base alloys DMV 600 H, and DMV 617 mod. which possess an absolutely stable austenitic microstructure.

Despite differences in the mechanical and physical properties of the materials (shown in tables 3a, 3b and 3c) due to their chemical composition, there are certain similar characteristics that are attributable to their metallurgical face-centred cubic lattice structure.

MST designation	Heat treatment condition	Temperature (°C) Creep strength (MPa) after ...																	
		10,000 hours					100,000 hours					200,000 hours							
		550	600	650	700	750	550	600	650	700	750	550	600	650	700				
DMV 304 H	solution annealed	250	132	87	55	(34)	192	89	52	28	(15)	176	78	43	22				
DMV 304 HCu	solution annealed		600	650	700	750		600	650	700	750								
			240	160	101	61		182	116	68	37								
DMV 304 N	solution annealed	230	160	100	60	178	114	64	30										
DMV 316 H	solution annealed	250	175	111	65	175	120	69	34										
DMV 321 H	solution annealed	230	160	100	60	170	100	62	35	150	90	54	29						
DMV 347 H	solution annealed		600	650	700	750	800		600	650	700	750	800						
			115	70	45	28	(17)		65	39	22	13	(8)						
DMV 347 HFG	solution annealed		600	650	700	750		600	650	700	750								
			215	142	90	53		159	100	58	30								
DMV 4910	solution annealed	290	205	135	84	52	33	220	141	83	52	34	20	200	122	73	42	28	17
DMV 310 N	solution annealed		600	650	700	750		600	650	700	750								
			284	171	108	64		184	114	66	39								
DMV 800 H	solution annealed	225	140	97	69	160	95	63	44	143	83	55	38						
DMV 800 HT	solution annealed	57	41	28	18	12	7.9	35	25	17	9.9	6.2	(4.0)	30	21	13	8.0	4.5	3.2
DMV AC 66	solution annealed	80	46	24	10	6	(3.5)	52	27	16	5	3	(1.5)						
DMV 617	solution annealed	260	123	65	30	18	10	190	95	43	16	8.5	(4.5)						
DMV 600 H	solution annealed	138	163	29	17	13	97	42	17	9.5	7.0								
DMV 617 mod.	solution annealed	260	170	123	90	190	125	95	65										

Table 4: Creep properties

An example of how to read the table: creep strength of DMV AC 66 after 10,000 hours at 750°C is 46MPa. Values in brackets are extrapolated.

MST designation		C	Si	Mn	P	S	Cr	Ni	Mo	N	Others
DMV 304 H	min. max.	0.04 0.08	0.75	2.0	0.035	0.015	17.0 19.0	10.0 12.0			
DMV 304 HCu	min. max.	0.07 0.13	0.30	1.0	0.040	0.010	17.0 19.0	7.5 10.5		0.05 0.12	Nb(Cb): 0.3 - 0.6; Cu: 2.5 - 3.5; Al: 0.003-0.030; B: 0.001-0.010
DMV 304 N	min. max.	0.04 0.07	0.75	2.0	0.035	0.015	17.0 19.0	9.5 11.5	0.20 0.50	0.10 0.18	
DMV 316 H	min. max.	0.04 0.08	0.75	2.0	0.035	0.015	16.0 18.0	12.0 14.0	2.0 2.5		
DMV 321 H	min. max.	0.04 0.10	0.75	2.0	0.035	0.015	17.0 18.5	9.5 11.5	0.60		Ti: 5xC - 0.80; B: 0.0015 - 0.0050
DMV 347 H	min. max.	0.04 0.08	0.75	2.0	0.035	0.015	17.0 19.0	9.0 12.0			Nb: 10xC - 1.0
DMV 347 HFG	min. max.	0.06 0.10	0.75	2.0	0.040	0.030	17.0 20.0	9.0 13.0			Nb(Cb) + Ta: 8xC - 1.0
DMV 4910	min. max.	0.04 0.07	0.75	2.0	0.035	0.015	16.0 18.0	12.0 14.0	2.0 2.8	0.10 0.18	B: 0.0015 - 0.0050
DMV 310 N	min. max.	0.04 0.10	0.75	2.0	0.030	0.030	24.0 26.0	17.0 23.0		0.15 0.35	Nb: 0.20 - 0.60
DMV 800 H	min. max.	0.05 0.10	0.70	1.5	0.015	0.010	19.0 22.0	30.0 34.0			Al: 0.25 - 0.65; Ti: 0.25 - 0.65; Co: max. 0.5
DMV 800 HT	min. max.	0.06 0.10	0.70	1.5	0.015	0.010	19.0 22.0	30.0 34.0			Al: 0.25 - 0.65; Ti: 0.25 - 0.65; Co: max. 0.5
DMV AC 66	min. max.	0.04 0.08	0.30	1.0	0.015	0.010	26.0 28.0	31.0 33.0			Nb: 0.6 - 1.0; Ce: 0.05 - 0.10; Al: max. 0.025
DMV 600 H	min. max.	0.06 0.08	0.50	1.0	0.015	0.015	14.0 17.0	72.0			Fe: 6.0 - 10.0
DMV 617	min. max.	0.05 0.10	0.70	0.7	0.012	0.008	20.0 23.0	8.0 10.0	Remainder		Co: 10.0 - 13.0; Ti: 0.2 - 0.5; Al: 0.6 - 1.5

Table 2: Chemical composition in %

MST designation	Heat treatment condition	R _{p0.2} (MPa) min.	R _{p1.0} (MPa) min.	Rm (MPa)	A longit. (%) min.	A transv. (%) min.	a _k longitudinal (J)	a _k transversal (J)
DMV 304 H	solution annealed	185	225	500 - 700	40	30	90	60
DMV 304 HCu	solution annealed	235	270	590 - 850	35		85	
DMV 304 N	solution annealed	240	275	500 - 700	35	30	90	60
DMV 316 H	solution annealed	205	245	490 - 690	35	30	90	60
DMV 321 H	solution annealed	195	235	490 - 680	35	30	90	60
DMV 347 H	solution annealed	205	240	510 - 740	35		85	
DMV 347 HFG	solution annealed	205	240	550 - 750	35		85	
DMV 4910	solution annealed	260	300	550 - 750	35	30	120	80
DMV 310 N	solution annealed	295	325	655 - 900	30		85	
DMV 800 H	solution annealed	170	200	500 - 750	35	30	120	80
DMV 800 HT	solution annealed	170	200	500 - 750	35	30	120	80
DMV AC 66	solution annealed	185	215	500 - 750	35		85	
DMV 600 H	solution annealed	180	210	500 - 700	35	150	100	
DMV 617 / DMV 617 mod.	solution annealed	300	350	700 - 950	35	150	100	

Table 3a: Mechanical properties at room temperature

MST designation	Heat treatment condition	R _{p0.2} (MPa) min. at (°C)								R _{p1.0} (MPa) min. at (°C)							
		100 °C	200 °C	300 °C	400 °C	500 °C	550 °C	600 °C	650 °C	100 °C	200 °C	300 °C	400 °C	500 °C	550 °C	600 °C	650 °C
DMV 304 H	solution annealed	157	127	108	98	88	83	78		191	157	137	127	118	113	108	
DMV 304 HCu	solution annealed	205	180	170	160	150	145	140		230	205	195	185	175	170	165	
DMV 304 N	solution annealed	185	150	130	120	110	105	100		220	175	150	140	130	125	120	
DMV 316 H	solution annealed	177	147	127	118	108	103	98		211	177	157	147	137	132	128	
DMV 321 H	solution annealed	162	142	132	123	113	108	103		201	181	172	162	152	147	142	
DMV 347 H	solution annealed	177	157	136	125	119	118			211	186	167	156	149	147		
DMV 347 HFG	solution annealed	182	163	152	143	136	134	131	126	217	198	187	173	161	159	156	151
DMV 4910	solution annealed	205	170	148	134	127	124	121		240	200	178	164	157	154	151	
DMV 310 N	solution annealed	240	205	190	180	170	165	160	160	265	230	210	200	190	185	180	180
DMV 800 H	solution annealed	140	115	95	85	80	75	75		160	135	115	105	100	95	95	
DMV 800 HT	solution annealed	140	115	95	85	80	75	75		160	135	115	105	100	95	95	
DMV AC 66	solution annealed	160	140	120	105	95	90	90		190	170	145	130	115	110	110	
DMV 600 H	solution annealed	170	160	150	150												
DMV 617 / DMV 617 mod.	solution annealed	270	230	220	210	200	195	190		300	260	250	240	225	220	210	

Table 3b: Mechanical properties at elevated temperatures

MST designation	Density (kg/m ³)	Modulus of dynamic elasticity (kN/mm ²) at (°C)						Coefficient of thermal mean linear expansion (10 ⁻⁶ /K) between 20°C and (°C)					Thermal conductivity (W/m K) at 20°C	Specific heat (J/kg K) at 20°C	Specific electrical resistivity (μΩm) at 20°C
		20	100	200	400	700	1,000	100	200	400	700	1,000			
DMV 304 H	7.80	198	192	183	167	142		16.3	16.9	17.8	18.7		17	450	0.70
DMV 304 HCu		189	182	174	156	134		16.4	17.1	17.8	18.6		15		
DMV 304 N	7.81	198	192	183	167	142		16.3	16.9	17.8	18.7		17	450	0.70
DMV 316 H	7.88	198	192	183	167	142		16.3	16.9	17.8	18.7		16	450	0.77
DMV 321 H	7.80	198	192	183	167	142		16.3	16.9	17.8	18.7		17	450	0.70
DMV 347 H	7.83	200						16.0	17.0	18.0			15	500	0.73
DMV 347 HFG		200	190	185	170	145		16.3	16.9	17.8	18.7		14		
DMV 4910	7.91	198	192	183	167	142		16.3	16.9	17.8	18.7		16	450	0.77
DMV 310 N		193	191	184	167	144		13.4	15.6	17.0	17.9		12		
DMV 800 H	7.97	197	191	184	170	148	127	15.4	16.0	16.8	17.9	19.0	12	460	0.99
DMV 800 HT	7.98	197	191	184	170	148	127	15.4	16.0	16.8	17.9	19.0	12	460	0.99
DMV AC 66	7.98	191	195	179	166	144	119	14.0	16.0	19.0	23.0	28.0	12	445	0.96
DMV 600 H	8.47	214	214	209	194	172	143	13.7	14.1	14.8	15.8	16.9	15	455	1.03
DMV 617 / DMV 617 mod.	8.57	215	215	211	192	169	143	12.4			15.1	16.9	10	420	1.22

Table 3c: Physical properties

Embrittlement

Besides creep rupture strength, ductility is an important factor governing the suitability of a material for a given application. Under long-term stress both stabilized and non-stabilized steels display lower values of reduction in area after fracture. This is due to the hardening effect of special carbide precipitates and metallic phases. However, high-nickel steels DMV 800 H, DMV 800 HT and DMV AC 66, as well as nickel base alloys DMV 600 H and DMV 617 mod., also show very good ductility values after long-term exposure to service stresses across the range of high-temperature applications.

High-temperature corrosion and oxidation

Although the loads that act on tubes in heat resistant materials are many and varied, they can be determined by calculation and can be controlled by appropriate materials selection and correct design. However, experience has shown that external influences occur during the service life of plants, which cannot be predicted at the planning and design stage, as they largely result from the actual operating conditions to which the tubes are exposed. Most of these influences are related to high-temperature corrosion. Within the limits of the permissible temperature ranges, heat resistant austenitic steels generally exhibit excellent resistance to combustion gases with sufficient excess air.

To withstand the service conditions, the sensitivity of the material to oxidation on the steam-side is an important factor. As temperature increases, the oxide scale is generally formed more quickly and with a greater thickness. The higher material loss leads to reduced wall thickness and therefore to an increase of stress, causing creep rupture. This can be compensated to a certain extent by an increased wall thickness. In addition, the oxide scale leads to an insulation of the tube material which increases the metal temperature. Increased metal temperatures again may accelerate corrosion and creep rates on the flue gas side. Moreover, spalling of the thicker oxide scales can occur during service. The build up of these scales may cause blockage at the tube bends. The resulting decrease in steam flow could create local overheating and may lead to failure. The scale might also lead to severe erosion damage in the turbine. There is also a risk of erosion on valve seats and turbine blades due to the exfoliated oxides during unit start up.

Chromium is the key element influencing the corrosion behaviour of steels. The sensitivity of the material to steam-side oxidation as well as fire-side corrosion is an important factor for use in the

field of boilers. The use of high sulphur coal makes the fire-side corrosion resistance of even higher importance. The corrosion rate is increased by the deposition of sulphides on the tube surface. In the range of 600 to 650 °C these sulphides are in liquid state. Free sulphur trioxide dissolves the protective oxide scale to form iron and chromium based sulphates which rapidly increases the corrosion rate. A sufficient amount of chromium is necessary in order to reform the chromia layer. The higher a material's chromium content, the better its temperature stability, and the more dense the diffusion barriers (oxide layers) that are formed to protect against aggressive media such as sulphur, chlorine, and melts. This means carburization (metal dusting) and nitration are suppressed. As previously mentioned, in addition to a material's resistance to oxidation, other influencing factors need to be considered which arise from actual plant operating conditions.

Regarding the scaling behaviour of superheater pipes in a conventional power station, the following influencing factors have to be taken into account when considering flue gases:

- flue gas temperature
- tube wall temperature
- tube position
- heat transfer by radiation
- fuel composition
- flue gas composition (e.g. reducing streaks)
- firing principle (e.g. dry or fused ash handling)
- ash content in flue gas
- erosion

These external influencing factors often determine the service life of a plant.

However, loads on the water or steam side can also be influenced by plant operating conditions (e.g. boiler water and feedwater quality). These negative factors can only be effectively counteracted by appropriate plant handling which, in turn, calls for comprehensive expertise.

Many years' experience in the use of austenitic tube materials have proved their superiority over ferritic steels. This experience is also confirmed by the chemical industry where austenitic steels are used for superheater pipes, headers and piping systems of power stations and have invariably shown good oxidation resistance on the flue gas side even after long-term exposure to service stresses. On the steam side, austenitic steels have been shown to offer significantly more favourable corrosion behaviour than ferritic high-temperature steels.

Shot peening

As the Cr content at the inner and outer tube surface determines the corrosion and oxidation behaviour, a technique was developed to save costly alloying elements and make enough Cr available to have an improved oxidation behaviour at the outer tube surface: Shot peening. DMV 304 HCu is one of the 18Cr-8Ni austenitic steels with a typical content of 18 wt.-% of chromium. The corrosion resistance is furthermore characterised by the microstructure of the material. The formation of a dense Cr₂O₃ layer is supported as DMV 304 HCu maintains a relatively fine grain size. Diffusion of chromium is much faster along the grain boundaries than through the grains, so the smaller grain size improves this diffusion. Furthermore, shot peening of the inner surface of the tubes will improve the formation of an effective oxide layer. Due to cold deformation within a small layer, the amount of defects such as twin boundaries in the microstructure is increased. The diffusion of chromium becomes faster resulting in the rapid formation of a protective Cr₂O₃ layer. Further increase in the thickness of the oxide scale is slowed after the initial formation of the Cr₂O₃ layer. It is then determined by the solid diffusion of chromium and oxygen through the bulk or along grain boundaries of the oxide.

Processing and fabrication information

Hot forming

Before hot forming or heat treatment, the surfaces of high-alloy austenitic materials must be cleansed of grease, oil and other contaminants. Any remaining substances could burn into the surface and significantly affect the outer appearance of tubes by producing stains and rough spots. In addition, carburization may occur which could considerably reduce the material's corrosion resistance and deformability. If hot forming is necessary, it should be performed in the temperature range of 800 - 1,150 °C on all high-alloy austenitic materials, with the following exceptions:

DMV 617	(2.4663)	900 - 1,200 °C
DMV 600 H	(2.4816)	900 - 1,230 °C

Induction bending

To counteract surface strain, tubes made from austenitic CrNi and CrNiMo steels require to be given a recrystallizing heat treatment before hot induction bending. This applies particularly to the niobium-stabilized variants whose surface must be machined after solution annealing.

Cold forming

The low yield strength and high ductility of austenitic stainless steels and nickel base alloys give them excellent cold forming characteristics. The cold hardening effect associated with high



reduction ratios should be neutralized by subsequent heat treatment and accelerated cooling.

After solution annealing, the materials should be allowed to cool in water or air or; in the case of thinner tube walls, in air or in a protective atmosphere. Old forming involving reduction ratios in excess of 15 % should always be followed by a heat treatment process (solution annealing).

Machining

As austenitic steels typically possess very low thermal conductivity, sufficient coolant must be provided when machining these materials. These steels also have a tendency to cold harden if blunt tools are used, which can lead to machining finish problems. It is therefore essential that adequate coolant, sharp tools and the careful setting of the cutting depths and speeds are maintained.

Welding

Heat resistant high-alloy materials are readily weldable using an inert gas welding technique (TIG, MIG) or manual electric welding in conjunction with welding materials of proven suitability. The manufacturer's processing guidelines have to be observed. Heat input during welding should be kept as low as possible. The interpass temperature should not exceed 200 °C.



Heat treatment

Apost-weld heat treatment is generally not required. For components with non-homogeneous stress distribution, stress relieving at 1,000°C may be desirable. Different temperature zones in a plant often require dissimilar materials, e.g. ferritic or martensitic steels, to be joined with austenitic materials. The welding materials and parameters used for such dissimilar welds must be carefully selected to match the properties of both materials. This also applies to post-weld heat treatment (if required).

Our stainless steels and nickel base alloys listed in this brochure all exhibit the high strength characteristics over a wide temperature range whilst providing excellent resistance to aggressive media in boilers and superheater pipes under both short-term and long-term stress. In addition, their physical properties and processing characteristics have typically helped to improve the efficiency and reliability of power stations over a long service life.

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