



**MANNESMANN**  
**STAINLESS TUBES**

A Member of the Salzgitter Group

# DMV 304 HCu



**Boiler Grade DMV 304 HCu**

<b>1 Introduction</b>	<b>4</b>
1.1 Salzgitter Mannesmann Stainless Tubes	4
1.2 DMV 304 HCu	5
1.3 Trend	5
1.4 Specifications (Standards)	6
1.5 Available Sizes	6
1.6 Special Features	6
<b>2 Material Properties</b>	<b>8</b>
2.1 Microstructure	8
2.2 Material properties according to ASME	9
2.2.1 Chemical composition	9
2.2.2 Mechanical properties	9
2.3 Material properties according to VdTÜV	11
2.3.1 Chemical composition	11
2.3.2 Tensile properties	12
2.3.3 Creep strength	13
2.3.4 Impact resistance	14
2.3.5 Physical properties	15
2.4 High temperature properties – Mechanism	16
2.4.1 High temperature and creep rupture strength	16
2.4.2 Microstructure stability	17
2.5 Corrosion resistance	18
<b>3 Fabrication</b>	<b>20</b>
3.1 Tube bending	20
3.2 Welding	20
<b>4 References</b>	<b>22</b>

# 1 Introduction



Headquarters Mülheim an der Ruhr, Germany

## 1.1 Salzgitter Mannesmann Stainless Tubes

Salzgitter Mannesmann Stainless Tubes is one of the leading manufacturers of seamless stainless steel and nickel alloy tubes and pipes. Our company has one of the largest product portfolios in this sector.

Our top quality products and efficient service contribute to the long-term success of our customers. Our top priority is to establish and maintain positive long-term relationships with our business partners.

In order to support you in the stockist and project business, with good quality, innovative materials and modern production technologies, our experts are constantly working

to keep up with all the latest trends.

As a company operating successfully on an international level, we unite many nationalities and cultures under one banner. Our network collaborates closely in all aspects of procurement, sales, production and logistics. Since our foundation as a joint venture, we hold our position in the top league of companies in this sector.

We are a member of the powerful Salzgitter Group and our stainless steel and nickel base products are an important addition to the Group's overall product range. Thanks to our impressive product portfolio, we can open up attractive growth prospects.

## 1.2 DMV 304 HCu

Our tubes and pipes are primarily used for boilers in thermal power plants and the energy sector. High temperature strength has become one of the most important attributes for the application of boiler tubes. At the same time, economic aspects play a decisive role. The 18Cr-8Ni steel grade 304 is a conventional austenitic stainless steel. With requirements for higher steam temperatures to increase the efficiency of power plants, the creep resistance of this steel is not sufficient today. Through the addition of about 3 wt.-% of copper, increased carbon content and certain amounts of niobium and nitrogen, the elevated temperature strength and especially the creep properties are improved in the grade DMV 304 HCu. The addition of nitrogen leads to a solid-solution strengthening of the material. This increases the allowable tensile stresses. The allowable stresses under creep conditions are mainly increased by the precipitation of a Cu-rich phase in the matrix. During service this phase is precipitating as well as the niobium carbonitride phase. The high temperature oxidation resistance is improved by shot peening of the inner tube surface. By this, a high density of grain and twin boundaries is created close to the surface. The chromium diffusion to the surface is accelerated and the formation of an adherent and dense  $\text{Cr}_2\text{O}_3$  layer is enhanced. This protective layer reduces further oxidation to a minimum. DMV 304 HCu beneficially utilises precipitation hardening to improve especially the creep

properties of conventional 18Cr-8Ni austenitic stainless steels. Using this effect an economic material for tube applications between 600 and 650 °C is provided.

## 1.3 Trend

Efficiency is a major criterion in defining the performance of power plants and boilers. Increasing the efficiency essentially results in a reduction of the fuel consumption and thus  $\text{CO}_2$  emissions, which is a big challenge at the present time. Efficiency is directly linked to the steam temperature and pressure. Target service conditions are currently steam temperatures above 600 °C or 1110 °F and pressures of more than 300 bar or 4,350 psi. The materials must withstand these conditions throughout the whole service life of the component. This results in higher demands on creep resistance, elevated temperature strength and high temperature corrosion resistance. The thickness of the oxide layer inside the tubes may increase. Thick oxide scales are more susceptible to spalling, which can cause blockage in the superheater tubes. Furthermore, higher steam temperatures will lead to higher material temperatures, resulting in a higher creep strength demand. This aspect is specifically addressed and improved by the copper addition in DMV 304 HCu material compared to the conventional austenitic grade 304. In future, steel development will continue to follow the new demands and challenges of boiler applications. It is widely expected

# 1 Introduction

that new power plants will run at even higher temperatures and pressures. Different steels and nickel based alloys already indicate the development for this future application, such as DMV 310N (for design temperatures up to 670 °C), DMV 617 and DMV 263 (for design temperatures up to 770 °C). All of these alloys contain higher nickel and chromium contents in order to meet the requirements for higher application temperatures and are thus more expensive.

## 1.4 Specifications (Standards)

DMV 304 HCu fulfils the requirements of the following specifications:

- 1.4907 (X10CrNiCu Nb 18 9 3), according to EN 10216-5, European Standard
- 18Cr-9Ni-3Cu-Nb-N according to ASME SA-213, US Standard
- ASME Code Case 2328-1 (03.2003), United States
- VdTÜV Material data sheet 550 (09.2003), Federal Republic of Germany

## 1.5 Available Sizes

DMV 304 HCu austenitic stainless steel is used to manufacture seamless austenitic reheater and superheater boiler tubes. This grade is suitable for all commonly required austenitic reheater and superheater boiler tube sizes and also in the most advanced coal fired power stations using steam temperatures up to approximately 640 °C

(1185 °F) in supercritical and ultra supercritical vessel designs.

Following VdTÜV material data sheet 550 (09.2003), a maximum outside diameter of 65 mm and a maximum wall thickness of 12.5 mm is available (standard size range according to EN-ISO 1127 as well as other sizes upon request).

## 1.6 Special Features

- DMV 304 HCu is an austenitic stainless steel with improved elevated temperature strength and especially creep resistance, which is attained by the addition of **copper**, niobium and nitrogen compared to the conventional 18Cr-8Ni austenitic grade 304.
- **Production route of DMV 304 HCu:**  
The material is first subjected to a hot forming process (hot extrusion). Subsequently, cold finishing is carried out on the material, followed by solution annealing at a temperature between 1100 °C and 1180 °C (2010 °F and 2155 °F). Finally, shot peening of the inner surface of the boiler tubes is performed, if requested.
- DMV 304 HCu has high **creep rupture strength** 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 (1075 and 1185 °F).
- The steam-side oxidation resistance of DMV 304 HCu is increased by **shot peening**.

An enhanced Cr transport to the surfaces results in an adherent and protective  $\text{Cr}_2\text{O}_3$  layer.

- Small amounts of nitrogen and niobium combined with an increased carbon content further improves the properties: the effects of a certain pinning of the grain size during solution-annealing (grain size 7 or finer), solid-solution strengthening of nitrogen (before creep), and precipitation hardening during creep loading are used.
- An **economical material** for boiler tube applications is produced, with good creep properties and sufficient steam-side oxidation resistance.



## 2 Material Properties

### 2.1 Microstructure

The steel grade DMV 304 HCu is an 18Cr-8Ni austenitic stainless steel. Differences in material properties and especially in the creep resistance compared to the conventional grade DMV 304 are mainly achieved by addition of about 3 wt.-% of copper. The formation of fine Cu-rich precipitates during service leads to an increased creep strength by the mechanism of precipitation hardening. Additionally, an increased carbon, niobium and nitrogen content are effective compared to the conventional grade. The material properties are influenced by the precipitation of niobium carbonitrides,  $M_{23}C_6$  carbides and NbCrN. A high phase stability during long-term aging is achieved [1].

The production of boiler tubes is divided into three main processing steps. A first thermal treatment is performed during the hot extrusion of the material. This is followed by cold deformation to produce the final dimensions of the tube (cold pilgering or cold drawing). A final heat treatment completes the production route. During this solution treatment, the precipitates are mainly dissolved in the austenitic matrix material. However, a certain amount of carbonitride precipitates remains, restricting the grain coarsening by pinning the grain boundaries. Thus, the grain size is limited as far as ASTM No. 7. Except for the small amount of niobium carbonitrides, the other elements and especially the copper are dissolved in the austenitic matrix. The fully

austenitic microstructure of DMV 304 HCu in as-delivered condition is shown in Figure 1.

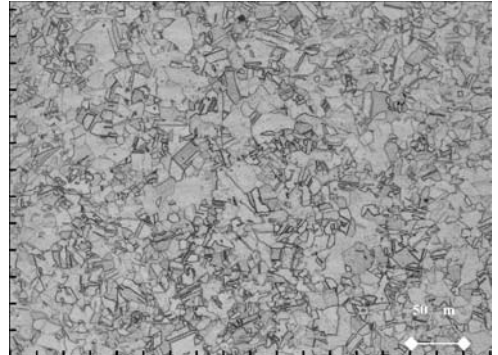


Figure 1: Microstructure of DMV 304 HCu in solution-annealed condition.

In the solution-annealed condition the dissolved nitrogen increases the tensile strength at room temperature and elevated temperatures by the solid solution-strengthening effect. Under creep conditions in service, precipitation of phases such as  $M_{23}C_6$ , niobium carbonitride and NbCrN starts to improve the creep resistance. However, the main effect on the creep rupture control is due to the coherent precipitation of a very fine Cu-rich phase in grains. This effect is most apparent after complete dissolution of copper during solution annealing. Thus, the full amount of copper can be utilised during exposure to creep conditions.

DMV 304 HCu exhibits a stable microstructure after long-term exposure at elevated temperatures with only small amounts of brittle intermetallic phases such as sigma-

phase [1]. Nevertheless, a certain coarsening of the Cu-rich phases takes place during long-term service. If the strengthening effect is attributed to the coherency strain of the precipitates, the Cu-rich phases are less effective if coarsening is too rapid. Thus, an optimum copper content of 3 wt.-% is reached [2]. The microstructure of DMV 304 HCu after creep rupture test at 600 °C and 303 MPa is shown in Figure 2. This shows typical creep damage in form of microcracks orientated perpendicular to the stress direction.

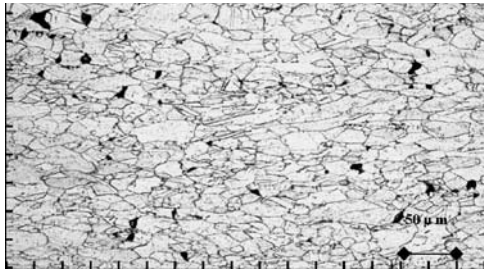


Figure 2: Microstructure of DMV 304 HCu after failure in creep rupture test (600 °C, 303 MPa, 2009 h).

[wt-%]	C	Mn	P	S	Si	Ni	Cr	Cu	Nb	N	Al	B
<b>min.</b>	0.07	-	-	-	-	7.5	17.0	2.50	0.30	0.05	0.003	0.001
<b>max.</b>	0.13	1.0	0.04	0.01	0.3	10.5	19.0	3.50	0.60	0.12	0.030	0.010

Table 1: Chemical composition of DMV 304 HCu.

	ksi	MPa	%
<b>Minimum yield strength</b>	34	235	-
<b>Minimum tensile strength</b>	85	590	-
<b>Minimum elongation in 2 inch</b>	-	-	35

Table 2: Mechanical property requirements in solution-annealed condition according to ASME Code Case 2328-1.

## 2.2 Material properties according to ASME

The material meets the applicable requirements of ASME SA-213 specifications.

The required material properties are further described in the ASME Code Case 2328-1: 18Cr-9Ni-3Cu-Nb-N.

### 2.2.1 Chemical composition

The requirements with regard to chemical composition are summarised in Table 1. The composition given in the ASME Code Case is the same as that given for the cast analysis in the VdTÜV materials data sheet 550 (09.2003). A solution treatment at a temperature of at least 2,000 °F (1,100 °C) is performed before delivery.

### 2.2.2 Mechanical properties

Tensile properties at room temperature in the solution-annealed condition according to the ASME Code Case are given in Table 2.

Additionally, the hardness shall not exceed 219 HB (230 HV, 95 HRB).



## 2 Material Properties

Temperature °F	Maximum allowable stresses		Temperature °C	Maximum allowable stresses	
	ksi	ksi <sup>1)</sup>		MPa	MPa <sup>1)</sup>
-20 to 100	22.7	22.7	-30 to 40	157	157
200	19.8	22.7	65	144	157
300	18.2	22.7	100	135	157
400	17.1	22.7	150	126	157
500	16.3	21.9	200	119	157
600	15.6	21.1	250	113	153
650	15.3	20.7	300	109	147
700	15.1	20.4	325	107	145
750	14.9	20.1	350	106	143
800	14.6	19.8	375	104	140
850	14.4	19.5	400	103	139
900	14.2	19.2	425	101	137
950	14.0	18.9	459	99.9	135
1,000	13.8	18.6	475	98.5	133
1,050	13.6	18.3	500	97.2	131
1,100	13.4	18.1	525	95.9	129
1,150	13.2	14.7	550	94.6	128
1,200	11.4	11.4	575	93.4	126
1,250	8.7	8.7	600	92.3	121
1,300	6.5	6.5	625	91.3	97.9
1,350	4.7	4.7	650	78.0	78.0
1,400	3.3	3.3	675	61.1	61.1
1,450	2.2	2.2	700	46.9	46.9
1,500	1.5	1.5	725	35.3	35.3
-	-	-	750	25.9	25.9
-	-	-	775	18.5	18.5
-	-	-	800	12.9	12.9
-	-	-	825	8.9	8.9

<sup>1)</sup>slightly greater deformation acceptable

Table 3: Maximum allowable stresses at elevated temperatures according to ASME Code Case 2328-1, US customary units and SI metric units.

In the ASME Code Case 2328-1, the maximum allowable stress values at different temperatures are given (see Table 3, Figure 3). The maximum design temperature is 1,500 °F (815 °C). In the second column higher values are given for cases in which slightly greater deformation (1%) is acceptable. These values exceed 66.67 %, but do not exceed 90 % of the yield strength at temperature. The use of these stresses may

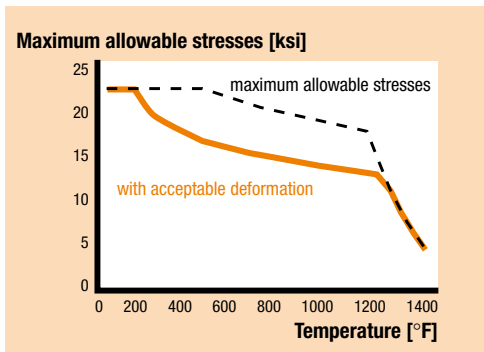


Figure 3: Maximum allowable stresses according to ASME Code Case 2328-1.

result in dimensional changes due to permanent strain. These stress values are not recommended for the flanges of gasketed joints or other applications where slight amounts of distortion can cause leakage or malfunction.

## 2.3 Material properties according to VdTÜV

In the following, material properties as given in the VdTÜV material data sheet 550 (09.2003) are summarised.

### 2.3.1 Chemical composition

The requirements with regard to chemical composition are given in Table 4. The composition given in the VdTÜV material data sheet for the heat analysis is the same as that given in the ASME Code Case 2328-1. According to standard practice in Europe, the requirements for the product analysis are slightly extended. Solution annealing of the finished tubes is carried out at a temperature between 1100 and 1180 °C (2010 to 2155 °F).

	[wt-%]	C	Mn	P	S	Si	Ni	Cr	Cu	Nb	N	Al	B
Cast analysis	min.	0.07	-	-	-	-	7.5	17.0	2.50	0.30	0.05	0.003	0.001
	max.	0.13	1.0	0.04	0.01	0.30	10.5	19.0	3.50	0.60	0.12	0.030	0.010
Part analysis	min.	-	-	-	-	-	7.4	16.8	2.45	0.25	0.04	0.003	0.0097
	max.	0.14	1.04	0.045	0.015	0.35	10.6	19.2	3.55	0.65	0.13	0.030	0.0103

Table 4: Chemical composition of DMV 304 HCu.

## 2 Material Properties

### 2.3.2 Tensile properties

Tensile properties at room temperature are given in Table 5. The values for proof strength are minimum values and are valid irrespective of location and position of the sample.

Tensile properties at elevated temperatures are presented in Table 6 and Figure 4. The 0.2 % and 1 % proof strength and the tensile

strength are summarised. The samples are taken in longitudinal direction. The given values are valid irrespective of location and position of the sample. The data for tensile strength at elevated temperature are guidelines. The improved tensile properties compared to conventional grade 304 are due to the solid solution strengthening effect of nitrogen [1].

	MPa	ksi <sup>1)</sup>	%
<b>0.2% proof strength, min.</b>	235	34.1	-
<b>1 % proof strength, min.</b>	270	39.2	-
<b>Tensile strength</b>	590 - 850	85.6 - 123	-
<b>Elongation at fracture</b>	-	-	35

<sup>1)</sup> calculated values

Table 5: Tensile properties at room temperature according to the VdTÜV material data sheet 550 (09.2003).

Temperature		0.2% proof strength		1 % proof strength		Tensile strength	
°C	°F <sup>1)</sup>	MPa	ksi <sup>1)</sup>	MPa	ksi <sup>1)</sup>	MPa	ksi <sup>1)</sup>
100	212	205	29.7	230	33.4	530	76.9
200	392	180	26.1	205	29.7	490	71.1
300	572	170	24.7	195	28.3	485	70.3
400	752	160	23.2	185	26.8	480	69.6
500	932	150	21.8	175	25.4	455	66.0
550	1022	145	21.0	170	24.7	440	63.8
600	1112	140	20.3	165	23.9	405	58.7
650	1202	135	19.6	160	23.2	370	53.7
700	1292	135	19.6	160	23.2	320	46.4
750	1382	125	18.1	150	21.8	280	40.6

<sup>1)</sup> calculated values

Table 6: Minimum proof strength and tensile strength at elevated temperatures according to the VdTÜV material data sheet 550 (09.2003).

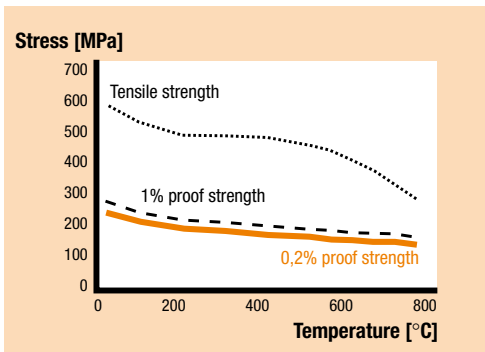


Figure 4: Minimum proof strength and tensile strength at elevated temperatures according to the VdTÜV material data sheet 550 (09.2003).

### 2.3.3 Creep strength

The creep strength values for 10,000 h and 100,000 h are summarised in Table 7. The datasets are evaluated data for long term values based on test results available to date. They are the average values of the existing scatter band. These datasets are checked and may be corrected from time to time in the VdTÜV material data sheet. It can be assumed that the lower limit of the scatter band is about 20 % lower than the given average.

Temperature		10,000 h		100,000 h	
°C	°F <sup>1)</sup>	MPa	ksi <sup>1)</sup>	MPa	ksi <sup>1)</sup>
600	1112	240	34.8	182	26.4
610	1130	222	32.2	165	23.9
620	1148	206	29.9	152	22.0
630	1166	192	27.8	139	20.2
640	1184	174	25.2	126	18.3
650	1202	160	23.2	116	16.8
660	1220	146	21.2	105	15.2
670	1238	134	19.4	96	13.9
680	1256	124	18.0	86	12.5
690	1274	114	16.5	78	11.3
700	1292	101	14.6	68	9.9
710	1310	92	13.3	61	8.8
720	1328	84	12.2	54	7.8
730	1346	76	11.0	48	7.0
740	1364	68	9.9	42	6.1
750	1382	61	8.8	37	5.4

<sup>1)</sup> calculated values

Table 7: Average creep strength values for 10,000 h and 100,000 h according to the VdTÜV material data sheet 550 (09.2003).

## 2 Material Properties

In Figure 5, the average values of the creep strength for 10,000 and 100,000 h are displayed together with the minimum values of the 0.2 % proof strength of DMV 304 HCu showing the typical intersection of these values.

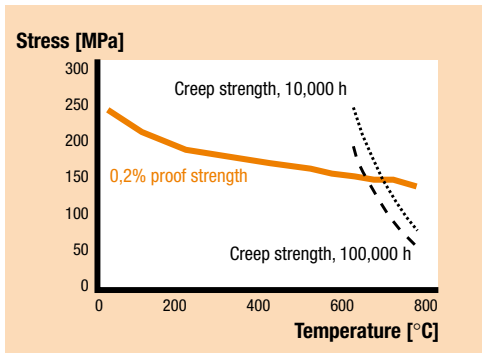


Figure 5: Creep strength for 10,000 and 100,000 h in comparison to the 0.2 % proof strength at elevated temperatures..

### 2.3.4 Impact resistance

According to the VdTÜV material data sheet 550 (09.2003), the average impact energy in longitudinal direction should be at least 85 J at room temperature. This value is the average of 3 specimens. Only one of the 3 results is permitted to fall below the required level, by a maximum of 30 %. The impact values drop significantly after a fairly short time of operation. After aging of the material between 500 and 750 °C (932 and 1382 °F), saturation is reached within 300 and 1000 h. Thereafter, stable values were found until a test duration of  $10^4$  hours [1]. Sufficiently good toughness is indicated in these aging conditions. However, in the VdTÜV material data sheet 550 (09.2003) it is stated that the typically decreased impact value should be considered during downtimes, hydrostatic pressure tests etc. For instance, fast start-up cycles should be avoided.

### 2.3.5 Physical properties

In Table 8 and Figure 6, the dynamic modulus of elasticity is given. The summarised values are guidelines.

Temperature		Modulus of elasticity	
°C	°F <sup>1)</sup>	10 <sup>3</sup> MPa	10 <sup>3</sup> ksi <sup>1)</sup>
20	68	189	27.4
100	212	182	26.4
200	392	174	25.2
300	572	165	23.9
400	752	156	22.6
500	932	149	21.6
600	1112	141	20.4
700	1292	134	19.4
750	1382	130	18.9

<sup>1)</sup>calculated values

Table 8: Modulus of elasticity according to the VdTÜV material data sheet 550 (09.2003).

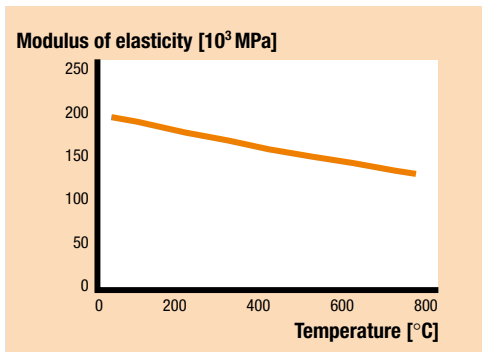


Figure 6: Modulus of elasticity according to the VdTÜV material data sheet 550 (09.2003).

The coefficient of thermal expansion is given in Table 9 and Figure 7. The reference temperature is 20 °C. The given values are guidelines.

Temperature: between 20 °C and ...		Coefficient of thermal expansion	
°C	°F <sup>1)</sup>	10 <sup>-6</sup> / K	10 <sup>-6</sup> / °F <sup>1)</sup>
100	212	16.4	9.1
200	392	17.1	9.5
300	572	17.5	9.7
400	752	17.8	9.9
500	932	18.1	10.1
600	1112	18.4	10.2
700	1292	18.6	10.3
750	1382	18.7	10.4

<sup>1)</sup>calculated values

Table 9: Coefficient of thermal expansion (reference temperature 20 °C (68 °F)) according to the VdTÜV material data sheet 550 (09.2003).

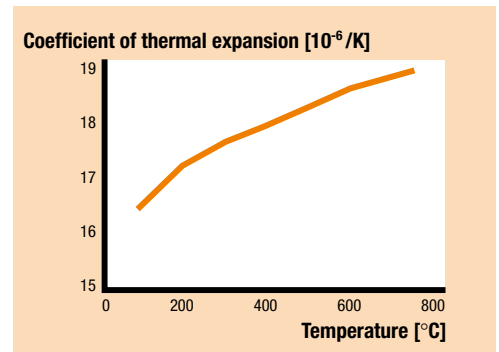


Figure 7: Coefficient of thermal expansion (reference temperature 20 °C (68 °F)) according to the VdTÜV material data sheet 550 (09.2003).

## 2 Material Properties

In Table 10 and Figure 8, the values of thermal conductivity are summarised. Here again, the given values are again guidelines.

Temperature		Thermal conductivity	
°C	°F <sup>1)</sup>	W / (m·K)	Btu / (ft·h·°F) <sup>1)</sup>
20	68	14.5	8.4
100	212	16.2	9.4
200	392	19.4	11.2
300	572	21.5	12.4
400	752	23.0	13.3
500	932	25.2	14.6
600	1112	28.6	16.5
700	1292	31.0	17.9
750	1382	31.0	17.9

<sup>1)</sup>calculated values

Table 10: Thermal conductivity according to the VdTÜV material data sheet 550 (09.2003).

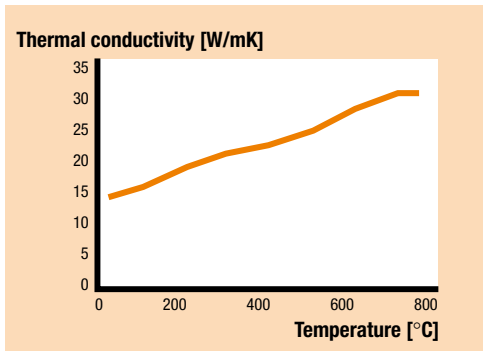


Figure 8: Thermal conductivity according to the VdTÜV material data sheet 550 (09.2003).

### 2.4 High temperature properties – Mechanism

The efficiency of conventional steam power plants depends to a large degree on the steam temperature and the pressure. Steam temperature has increased by about 60 °C (110 °F) in the last 30 years and a further increase of up to 100 °C (180 °F) is expected in the next 30 years. The sensitivity of the utilised materials to creep is one of the major limiting factors for further increase in steam temperature. However, the selection of a suitable material is always accompanied by economic considerations. The aim being a long-term stability of all components for the lowest possible financial outlay. Thus, materials are chosen which are precisely tailored to exactly fulfil the requirements for a specific component. Compared to the conventional grade 304 the material DMV 304 HCu is optimised by the addition of further alloying elements to better withstand creep loading in the temperature range between 580 and 640 °C (1075 and 1185 °F). Relatively inexpensive elements such as copper, niobium and nitrogen are used to achieve an economic alternative to other grades with increased contents of chromium and nickel.

#### 2.4.1 High temperature and creep rupture strength

Improved mechanical properties, especially high-temperature strength and creep strength, can be achieved by solution strengthening or precipitation hardening

effects. Both effects are used in DMV 304 HCu for different reasons. In the solution-annealed condition, only a small amount of niobium carbonitrides is precipitated in the material. Thus, just a restricted precipitation hardening effect is reached. In connection with the solid-solution strengthening by nitrogen, a sufficient tensile strength at room temperature and at elevated temperatures is reached even before aging during exposure to creep conditions. During service, the precipitation hardening effect is improved by the formation of precipitates such as  $M_{23}C_6$ , niobium carbonitride and NbCrN. During precipitation of the nitrides, the amount of dissolved nitrogen in the austenitic matrix is reduced which also decreases the solid-solution strengthening. Nevertheless, the tensile strength at elevated temperature is slightly increased with longer aging times at elevated temperature [1].

The largest effect on the creep resistance is attributed to the formation of very fine Cu-rich precipitates. These are precipitating in the grain interiors during service and their diameter ranges from 15 to 50 nm [1-4]. In a comparable steel grade this precipitation is found to be independent of the formation of other precipitates such as carbides making it possible to use both effects simultaneously [2]. While the grain boundaries are strengthened by carbide precipitates, Cu-rich precipitates will increase the strength of the matrix. This effect is attributed to the influence of the coherency strain around the particles gener-

ated by the lower flow stress of the precipitates compared to the matrix [2].

#### 2.4.2 Microstructure stability

Precipitation can usually be divided into three stages: nucleation, growth and coarsening. After nucleation, growth of the precipitates (carbides, nitrides as well as the Cu-rich phase) takes place. When the supersaturation of the austenitic matrix is mostly reduced, the volume fraction of these precipitates remains constant. A coarsening of the precipitates takes place which is described by the so-called Ostwald ripening process. For the efficiency of the Cu-rich precipitates there is a critical diameter in the range of about 30 nm (for pure Cu in an austenitic matrix) at which the coherency with the austenitic matrix is lost [2]. The precipitation strengthening was considered to be less effective, if the coherency limit of the Cu-rich precipitates is exceeded. Thus, the retained presence of very fine coherent Cu-rich precipitates over extended service periods is the goal. Coarsening is also influenced by the amount of alloying elements and thus the amount of precipitates formed. The distance between the precipitates is lower if more precipitates are formed, resulting in an increased kinetic for the coarsening. Thus, the optimum copper content is found to be 3 wt.-% [2,3]. The effect of Cu-rich precipitates on the creep properties is also restricted by the service temperature. At elevated temperatures above about



## 2 Material Properties

750 °C, the precipitation and coarsening is faster. Thus, the efficiency of the precipitates is restricted to short times until the coherency is lost. At still higher temperatures of about 850 °C no formation of the Cu-rich phase takes place any longer [2].

The formation of carbides and nitrides during service is also beneficial to the creep resistance. In particular, the formation of niobium carbonitrides within the grains is important. The formation of carbides such as  $M_{23}C_6$  occurs preferentially on grain boundaries which, as a result, are strengthened. However, depletion of carbon in the matrix promotes the formation of intermetallic phases such as sigma phase. Furthermore, during the formation of the chromium carbide  $M_{23}C_6$  a remarkable amount of chromium is removed from the matrix and is not available to restrict corrosion. The formation of intermetallic phases, firstly sigma phase, leads to a drop in ductility and toughness and causes embrittlement of the material [5]. The sigma phase is an intermetallic phase consisting mainly of iron and chromium. During service conditions, the formation of this phase takes place according to the thermodynamic stability and the kinetics of precipitation. Thus, the kinetic effects of the formation are of high importance. They are influenced by the composition of the alloy and the grain size (diffusion along the grain boundaries is much faster than through the

grains). Furthermore, the size and distribution of the phase is important [6]. These effects are considered during optimisation of the alloy.

### 2.5 Corrosion resistance

To withstand the service conditions, the sensitivity of the material to oxidation on the steam-side is an important factor [2]. 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 content is an important value in determining the corrosion resistance of

austenitic stainless steels. Its purpose is the formation of a protective and adherent  $\text{Cr}_2\text{O}_3$  layer which slows down the further oxidation. 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  $\text{Cr}_2\text{O}_3$  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 blasting or 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 (about 50  $\mu\text{m}$ ), 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  $\text{Cr}_2\text{O}_3$  layer. Further increase in the thickness of the oxide scale is slowed after the initial formation of the  $\text{Cr}_2\text{O}_3$  layer. It is then determined by the solid diffusion of chromium and oxygen through the bulk or along grain boundaries of the oxide. This is relatively low in the dense structure of  $\text{Cr}_2\text{O}_3$ . The formation of other oxides such as the spinel-type scale of  $(\text{Fe},\text{Cr})_3\text{O}_4$ , which is formed if insufficient chromium is transported, exhibits a higher permeability resulting in stronger oxidation.

The oxide scales usually consist of an inner chromium-rich and an outer iron-rich layer. Corrosion resistance of DMV 304 HCu can be further improved by using shot peening technology to enhance the chromium diffusion during the formation phase of the oxide layers.

## 3 Fabrication

### 3.1 Tube bending

Boiler tubes manufactured in steel grade DMV 304 HCu are generally suitable for cold and hot deformation. If hot forming is not performed using a controlled temperature process between 1100°C and 1150°C (2010 and 2100 °F), an additional solution-annealing is required. Cold-formed tubes to be used under creep conditions also have to be additionally solution-annealed, if the cold deformation is too high.

If cold deformation exceeds the values given in Table 11, additional solution annealing after deformation is mandatory.

selection of filler material becomes an important factor for good properties of the welded component. It should have a high corrosion resistance and even better mechanical properties than the base material. To avoid hot cracks in the weld metal, the processes recommended by the filler metal producers have to be observed.

The material DMV 304 HCu is weldable using state-of-the-art technologies. The following fusion welding techniques are possible: metal gas-shielded welding with welding wires, welding sticks or with cored wire electrodes and metal arc welding with lime alkaline enclosed electrodes. It is necessary to use ap-

Norm	Max. cold deformation	Radius to wall thickness ratio	Additional solution annealing temperature
VdTÜV Datasheet 550	>25%	≤ 2,0	1100-1150°C (2012-2102°F)

In order to maintain high corrosion resistance, a new solution-annealing is recommended even after a small degree of cold deformation.

### 3.2 Welding

The weld joint is considered to be one of the weakest areas in a fabricated component. Therefore it is necessary to consider the characteristics of the weld material to avoid failures. Weldability is usually characterised by resistance to hot cracking and the mechanical properties of the weld joints. The

proved filler materials which are also tested at the foreseen application temperature. Most common filler wires are Ni-materials based on alloy 617. Preheating and heat treatment after the welding process in the fabrication of DMV 304 HCu is not mandatory. However, if the material is sensitised after welding, a post welding treatment (solution treatment) can be done to restore the properties, mainly to increase the wet corrosion resistance [VdTÜV material data sheet 550 (09.2003)]. Different mechanical testing is performed at weld joints, i.e. mainly elevated temperature



tensile test, weld joint bending test, hardness measurement and V-notched charpy impact tests. In addition, the creep behaviour has to be tested. In order to prevent premature failure of weld joints, the weld metal has to have a creep strength equal to or better than the base material.

Generally, austenitic stainless steels have a high susceptibility to hot cracking in the weld. Intergranular reheat cracking is also reported in stabilised austenitic steels. In the heat affected zone after fast cooling from weld-

ing temperature, finely precipitated niobium carbonitrides generate residual stresses [8]. Thus, the weldability of DMV 304 HCu is for example considered to be better than that of DMV 347 HFG because of the lower niobium content. The weld joints can show the same high temperature tensile properties and creep rupture strength as those of the base material using an optimised filler metal [1].

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