Low alloy CrMo(V) steel plates for petrochemical reactors
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Introduction

Wherever high temperatures and/or high hydrogen partial pressures in the processes are required, CrMo steels have been used for more than 50 years. Due to changing process parameters in chemical and petrochemical processes these steel grades have been developed to enhanced properties.

- **conventional CrMo steels:** ASTM A387 Gr.11 Cl 1 and 2 or Gr. 22 Cl. 2 or 13CrMo4-5 or 10CrMo9-10 acc. EN 10028 part2

- **enhanced CrMo steels:** quenched and tempered steels with increased mechanical properties, e.g. ASTM A 542A/B 3/4/4a or 12CrMo9-10 acc. EN 10028 part 2

- **new generation of CrMo steels:** Vanadium modified CrMo-steels, e.g. ASTM A542 D4a or 13CrMoV9-10 acc. to EN 10028 part 2.
A broad variety of CrMo(V) steels is commercially available

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<th>Type</th>
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<th>Standards</th>
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<td>10CrMo9-10</td>
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<td>EN 10028-2: 2003</td>
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<td>12CrMoV12-10</td>
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Low alloy CrMo(V) steel plates for petrochemical reactors
Application and trends for the use of CrMo(V) steels

• typical applications are hydrotreating reactors

• operating temperatures up to 480 °C

• hydrogen partial pressures up to 180 bar or even more

Trends:

• ever bigger and heavier reactors (already more than 1000t per unit)

• higher operating temperatures and pressures resulting in higher wall thicknesses

• increasing demand due to expansion or new construction of plants
Developments in different aspects between 2000 and 2008

Example: 2½Cr1Mo steels

- dramatic increase of deliveries
- deliveries in thickness over 100mm were increased even more than the overall deliveries for these grades
- deliveries in N+AC+T condition were also increased dramatically
- market is very tight as demand is fast rising and only few manufacturers are able to meet the very high quality standards requested
Factors contributing to more sophisticated steel plates

- strong safety requirements for core units designed from CrMo(V) steels
- increasing thickness with high demand in thickness over 100mm
- larger dimensions to allow for more freedom in vessel design
- PWHT requirements including 3 or often even 4 cycles
- chemical restrictions exceeding those of the standards
- specifying J- and X-factor for ultra clean steels
- specifying toughness values at low temperatures in combination with PWHT
- additional requirements in regard to grain size
- hardness requirements
- specifying step cooling test
- additional tensile test at elevated temperatures
- ...

Many additional requirements; partly interfering each other
CrMo-plate delivery dimensions of Dillinger Hütte GTS

- **N + AC + T (Q + T)**:
  - up to 28 t
- **N + T**:
  - up to 37 t

Up to 42 t upon agreement.

Maximum thickness is often limited by requirements from specifications.

Low alloy CrMo(V) steel plates for petrochemical reactors
Common additional requirements for different CrMo(V) grades

- Hardness
- Step Cooling

> 100 mm

- J- / X-Factor
- Ch-V + PWHT

- 1Cr ½Mo
- 1¼Cr ½Mo
- 2¼Cr 1Mo
- 2¼Cr 1Mo ¼V
Concept of the Hollomon-Parameter (HP)

- The metallurgical effect of tempering and PWHT on the mechanical properties of steel can be combined by the HP-Parameter \((T \leq A_{C1})\)

\[
HP = T \times (20 + \log t) \times 10^{-3} \quad (T \text{ in K, } t \text{ in h})^*
\]

- Different heat treatment combinations of tempering and PWHT parameters leading to the same HP  
  \(\Rightarrow\) equivalent effect on the corresponding mechanical properties

- Destination of the acceptable values of the mechanical properties in dependence of heat treatment

- Optimization of the steel design

- Additional information and calculating program under:  
  www.dillinger.de/hollomon/hollomon.shtml.en

* If heating and cooling shall also be included the formula is getting more complex
Description of a heat treatment cycle by the Hollomon Parameter:

\[
HP = T (+ 273) \left[ \log \left( \frac{T (+ 273)}{2.3 \times K_h (20 - \log K_h)} \right) + t + \frac{T (+ 273)}{2.3 \times K_c (20 - \log K_c)} \right] + 20 \times 10^{-3}
\]

*) holding time starts when reaching temperature over the whole cross section

\( T \) \( K_h \) \( K_c \) \( t \)

- Holding Temperature \( [^\circ C] \)
- Heating rate \( [^\circ C/h] \)
- Cooling rate \( [^\circ C/h] \)
- Holding time \( [h]^* \)
Equivalence of Tempering and PWHT on Hollomon Parameter:

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<td>700°C/250Min.</td>
<td>670°C/180Min.</td>
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<tr>
<td>680°C/250Min.</td>
<td>680°C/600Min.</td>
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<tr>
<td>680°C/60Min.</td>
<td>690°C/300Min.+700°C/90Min.</td>
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<td>680°C/60Min.</td>
<td>675°C/600Min.+680°C/300Min.</td>
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General influence of heat treatment on mechanical properties

Before PWHT

After PWHT

Hollomon parameter

$A_V, R_m, R_{p0.2}$

$R_m$ before

$A_V$ before

$R_{p0.2}$ before

$R_m$ after

$A_V$ after

$R_{p0.2}$ after
Tensile strength in dependence of HP for CrMo and CrMoV steels

- 2,25CrMoV, t/4
- 2,25CrMoV, t/2
- 3CrMoV, t/4
- 3CrMoV, t/2
- 12CrMo 910

**CrMoV: acc. SA 542-D-4a**

**12CrMo 910 acc. EN 10028-2:2003**

**HP 20,8: Tempering +705 °C/10h**

**HP 21,11: Tempering +705 °C/30h**

**thickness: 200 mm**

**condition: N+AC+T**

Low alloy CrMo(V) steel plates for petrochemical reactors
Yield strength for CrMo and CrMoV steels

- 2½CrMoV, t/4
- 2 ¼ CrMoV, t/2
- 3CrMoV, t/4
- 3CrMoV, t/2
- 12CrMo 910 (2¼CrMo)

*CrMoV acc. SA 542-D-4a*

*HP 20,8: Tempering +705 °C/10h*

*HP 21,11: Tempering +705 °C/30h*

*CrMoV acc. SA 542-D-4a*

*12CrMo 910 acc. EN10028-2:2003*

Thickness: 200 mm
Condition: N+AC+T

Low alloy CrMo(V) steel plates for petrochemical reactors
CH-V-results vs HP compared between CrMo and CrMoV steels

- 2⅓CrMoV, t/4
- 3CrMoV, t/4
- 12CrMo 910 (2⅓CrMo)

Thickness: 200 mm
Condition: N+AC+T
Test temperature: -60°C
Test location: t/4

Charpy-V-transverse, $A_v$, mean [J] vs. HP

Low alloy CrMo(V) steel plates for petrochemical reactors
General observations when dealing with transition curves

![Graph showing transition curves and measured single values]
SA 387-11-2: Feasibility in dependence of HP, $R_m$, $R_e$, Ch-V, hardness and plate thickness of 1¼Cr steel

Low alloy CrMo(V) steel plates for petrochemical reactors
SA 387-22-2: Feasibility in dependence of HP, R_m, R_e, Ch-V, hardness and plate thickness of 2¼Cr steel
Offset in hardness between 2¼CrMo and 2¼CrMoV steels in dependence of delivery condition

Actual hardness distribution is depending on the steel design necessary to fulfill the overall requirements of the specification.

Low alloy CrMo(V) steel plates for petrochemical reactors
Aspects of interchangeability between 2¼Cr and 1¼Cr steels

• 1¼Cr½Mo Specs reflect more and more the attempt to replace 2¼Cr1Mo steels

• generally the 1¼Cr steels show a different toughness behaviour

• interchangeability is limited for different PWHT conditions and high thickness

• not only mech-tech properties but also other restrictions by the codes like e.g. listing in the Nelson curves are of importance
Tensile- and yield strength of enhanced 2¼CrMo steels (N+AC+T)

Thickness > 200 mm

- **12CrMo9-10**
  - **$R_{p0.2}$**
  - **$R_m$**

Tempering:
- **740 °C/30'**
- **PWHT-Min 690 °C/8h**
- **PWHT-Max 690 °C/24h**

- **Low alloy CrMo(V) steel plates for petrochemical reactors**

Verfasser/Dokument

DILLINGER HÜTTE GTS
Tensile- and yield strength of enhanced 2¼CrMo (V) steels (N+AC+T)

Thickness > 200 mm

Low alloy CrMo(V) steel plates for petrochemical reactors
Tensile- and yield strength of enhanced 2¼CrMo (V) steels (N+AC+T)

Thickness > 200 mm
Tensile- and yield strength of enhanced 2¼CrMo (V) steels (N+AC+T)

Thickness > 200 mm

Tempering 715 °C/250'
PWHT-Min 705 °C/8h
PWHT-Max 705 °C/24h

Low alloy CrMo(V) steel plates for petrochemical reactors
Estimated impact toughness of enhanced 2¼CrMo(V) steels (N+AC+T)
Hot tensile properties (transverse, 1/4 thickness)

- plate thickness: 200 mm
- heat treatment: N+AC+T

2¼CrMoV acc. EN 10028 part 2
12CrMo 910 acc. EN 10028 part 2

Testing temperature [°C]
Hot tensile properties (transverse, 1/4 thickness)

- **2¼CrMoV, R_m**
- **3CrMoV, R_m**
- **2¼CrMo, R_m, HP=21.0**
- **2¼CrMoV, R_{p0.2}**
- **3CrMoV, R_{p0.2}**
- **2¼CrMo, R_{p0.2}, HP=21.0**

Plate thickness: 200mm
Heat treatment: N+AC+T
Tensile testing at elevated temperatures - notes to ASME II D

Table U  

2001 SECTION II

NOTES TO TABLE U

GENERAL NOTES:

(a) The following abbreviations are used: ann., annealed; Cond., Condition; cond., condenser; Desig., Designation; fin., finished; fr., from; rel., relieved; rld., rolled; Smls., Seamless; Sol., Solution; Str., Strength; treat., treated; and Wld., Welded.

(b) The tabulated values of tensile strength are those which the Committee believes are suitable for use in design calculations. At temperatures above room temperature, the values of tensile strength tend toward an average or expected value which may be as much as 10% above the tensile strength trend curve adjusted to the minimum specified room temperature tensile strength. The tensile strength values do not correspond exactly to "average" as this term is applied to a statistical treatment of a homogeneous set of data. Neither the ASME Material Specifications nor the rules of Sections I, III, or VIII require elevated temperature testing for tensile strengths of production material for use in Code components. It is not intended that results of such tests, if performed, be compared with these tabulated tensile strength values for ASME Code acceptance/rejection purposes for materials. If some elevated temperature test results on production material appear lower than the tabulated values by a large amount (more than the typical variability of material and suggesting the possibility of some error), further investigation by retest or other means should be considered.

(c) Notes limiting applications of these materials appear in Tables 1A, 1B, 2A, 2B, 3, and 4.

Notes to Table U (like table Y1 also) state clearly:

• values given are for calculating purposes only

• ASME doesn’t require any hot tensile testing for production material

• If tests are performed, obtained values shall not be compared to tabulated values of table U for acceptance / rejection purposes
Comparison of real data and calculation values of ASME II D

ASME II D Table U: Tabulated values for calculation vs. measured values

TABLE U values are not suitable for acceptance purposes
Table Y-1

NOTES TO TABLE Y-1

GENERAL NOTES

(a) The following abbreviations are used: ann., annealed; cond., condensed; CW, cold worked; extr., extruded; fin., finished; fr., from; rel., relieved; rld., rolled; Smls., Seamless; Sol., Solution; SR, stress relieved; treat., treated; and Wld., Welded.

(b) The tabulated values of yield strength are those which the Committee believes are suitable for use in design calculations. At temperatures above room temperature, the yield strength values correspond to the yield strength trend curve adjusted to the minimum specified room temperature yield strength. The yield strength values do not correspond exactly to “minimum” or “average” as these terms are applied to a statistical treatment of a homogeneous set of data. Neither the ASME Material Specifications nor the rules of Section I, Section III, or Section VIII require elevated temperature testing for yield strengths of production material for use in Code components. It is not intended that results of such tests, if performed, be compared with these tabulated yield strength values for ASME Code acceptance/rejection purposes for materials. If some elevated temperature test results on production material appear lower than the tabulated values by a large amount (more than the typical variability of material and suggesting the possibility of some error), further investigation by retest or other means should be considered.

(c) Notes limiting applications of these materials appear in Tables 1A, 1B, 2A, 2B, 3, and 4.

(d) These values represent yield strength design values that are appropriate for use in any section of the ASME Boiler & Pressure Vessel Code in which the material is permitted and not otherwise restricted by applicability temperature limits, application limits, or notes.

(e) Where specifications, grades, classes, and types are listed in this Table, and where the material specification in Section II, Part A or Part B is a dual-unit specification (e.g., SA-516/SA-516M), the values listed in this Table shall be applicable to either the customary U.S. version of the material specification or the SI units version of the material specification. For example, the values listed for SA-516 Grade 70 shall be used when SA-516M Grade 485 is used in construction.

NOTES FOR SECTION VIII, DIVISION 3 APPLICATIONS

(1) This material is permitted only in wire form when used for wire-wound vessels and wire-wound frames as described in Article KD-9 of Section VIII, Division 3.

(2) Strength values for intermediate thickness may be interpolated.

(3) This material is permitted only when used as an inner layer in a vessel whose design meets the leak-before-burst criteria of KD-141 of Section VIII, Division 3.

(4) No welding is permitted on this material.

(5) This material has reduced toughness at room temperature after exposure at high temperature. The degree of embrittlement depends on composition, heat treatment, time, and temperature. The lowest temperature of concern is about 550°F. See Appendix A, A-360.

(6) For all design temperatures, the maximum hardness shall be Rockwell C35 immediately under thread roots. The hardness shall be taken on a flat area at least \( \frac{1}{4} \) in. across, prepared by removing threads; no more material than necessary shall be removed to prepare the flat area. Hardness determinations shall be made at the same frequency as tensile tests.
ASME II D tables U and Y1 tabulated vs. measured

Low alloy CrMo(V) steel plates for petrochemical reactors
Comparison of test results with Table U data for different grades

TABLE U values are not suitable for acceptance purposes
Basic connections between carbon content, tensile strength and toughness behaviour (unalloyed steel SA 516-70)

Estimated tensile strength versus of the Hollomon parameter for different carbon contents, plate thickness 40 mm. The minimum tensile strength acc. A516-70 is also shown in the diagram.
Low contents of As, Sb, Sn and P for improved temper embrittlement behaviour

- Temper embrittlement usually occurs in the temperature range between 370 and 580 °C.
- "Tramp" elements like P, Sn, Sb and As cause this phenomenon.
- J-factor and X-factor are commonly used as additional specification criteria.
- Modern steels with very low contents of "tramp" elements show no obvious correlation between J-/X-factor and embrittlement any more.
- For 2¼CrMo(V) steels usually the step cooling test is used to investigate the proneness to temper embrittlement.

![Intergranular crack](Image)
The mechanism of temper embrittlement

Conclusion:
- aim for low content of "embrittling" tramp elements
- specify J-value, X-value
- LD-Route + special steel refining advantageous, due to less tramp elements compared to EA process
- specify Step-cooling

"high safety" without danger of grain-boundary embrittlement!
Intergranular cracking and recommendations for avoidance

Strategies to avoid temper embrittlement

- aim for low content of „embrittling“ tramp elements
- specify J-factor, X-factor
- LD- Route (Basic Oxygen Furnace) + special steel refining is advantageous compared to electric arc process, due to less tramp elements
- specify Step-cooling test

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<th>special production</th>
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<td>P</td>
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<tr>
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<td>0,005</td>
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<tr>
<td>Sb</td>
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<td>0,001</td>
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* depending on Cr-content

** 80 for 2¼CrMoV

J- (Watanabe) Factor = (Mn + Si) * (P + Sn) * 10^4
X- (Bruscato) Factor = (10P + 5Sb + 4Sn + As) / 100

Special production: higher cost
Achievable P-contents as function of Cr-content for various process routes

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<th>Special converter process</th>
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<tr>
<td>Si</td>
<td>0.25 %</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>0.60 %</td>
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</tr>
<tr>
<td>Mo</td>
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</tr>
<tr>
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Graph:
- A: conventional process
- B: conventional process with heating in VD units
- C: special converter process

The graph shows the aimed P-content in ppm as a function of Cr-content [%].
Comparison of the tramp elements between EAF and LD-steelmaking

- **EAF with 70 % alloyed-rejects scrap + ferrous alloys**
- **EAF with sheet-metal scrap + ferrous alloys**
- **LD-steel BOF process**

**Mass content in ppm**

- **Arsenic (As)**
- **Tin (Sn)**
- **Antimony (Sb)**

- **EAF with 70 % alloyed-rejects scrap + ferrous alloys**
- **EAF with sheet-metal scrap + ferrous alloys**
- **LD-steel BOF process**
Ductility vs. Charpy notch toughness for 2¼CrMo

- Ductility and Charpy-values taken from randomly picked Dillinger orders in SA 387-22-2 at different temperatures. Plate thickness 134 & 208 (G&B) mm

A ductility requirement of 50% minimum would correspond to a toughness level of 140 to 150 J. A ductility value is usually offered for information. A slight decrease in toughness due to higher thickness can be observed.
• **Dillinger Hütte** offers 30ppm max. of total oxygen

• Oxygen is supposed to have a moderate negative impact on toughness, formability and machineability

• The higher oxygen content DH offers results from the requirement of low phosphorus to avoid embrittlement, which seems to be the main issue for these steels (keep J-factor low)

• Low phosphorus steels produced by the BOF route have to undergo a special additional treatment, which leads to a higher oxygen level of the heat, when entering the vacuum degasser

• During vacuum treatment it cannot be guaranteed in all cases that oxygen can be removed to the level obtained for “normal” production.

• The large majority of the steels will have max. 15 ppm after vacuum degassing, but some heats won’t show this amount

• Due to production risk restrictions given by the management DH only offers max. 30ppm of oxygen
Cumulative Oxygen content (example)

- Cumulative frequency in %
- O$_{\text{tot}}$ content final sample in ppm

- $+2\sigma$
- $+1\sigma$
- $-1\sigma$
- $-2\sigma$
Development of \([O]_{\text{tot}}\) during production for continuous casting and without special converter treatment

Steps after vacuum treatment are still very important to bring total oxygen further down
Step cooling - impact transition curve

\[ \Delta T_{\text{tot}} = 2.5 \times \Delta T_{\text{SC}} \]
Step cooling - heat treatment

step-cooling-treatment in accordance to EN 10028-2

test duration approx. 12 days + mechanical testing (including specimen preparation)

Low alloy CrMo(V) steel plates for petrochemical reactors
Step cooling on base metal - results

![Graph showing step cooling results](image)

**Graph Details**
- **ΔT after Step Cooling [K]**: The vertical axis represents the change in temperature after step cooling.
- **Tₜ₅₄[J] before Step Cooling [°C]**: The horizontal axis represents the temperature before step cooling.

**Key Points**
- Points below the line **TT + 2.5 x ΔT <= 10** are not fulfilled.
- Points above the line are fulfilled.

**Legend**
- Q+Δ
- N+Δ
- **TT + 2.5 x ΔT <= 10** curve

---

**Low alloy CrMo(V) steel plates for petrochemical reactors**

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Step cooling on base metal - results

![Graph showing step cooling results](image)

- **TT** before Step Cooling [°C]
- **ΔT** after Step Cooling [K]

- **Q+A**
- **N+A**

- **TT + 2.5 x ΔT ≤ 10**
- **TT + 3 x ΔT ≤ 10**

Legend:
- Blue: **Q+A**
- Orange: **N+A**

**Q+A** not fulfilled

**N+A** fulfilled

Low alloy CrMo(V) steel plates for petrochemical reactors
Advantages of Vanadium enhanced steels

- Higher strength / lighter weight reactors
- Improvement in temper embrittlement susceptibility
- Greater resistance to hydrogen attack (higher temperatures/H2 partial pressures are permissible)
- Greater resistance to hydrogen embrittlement
- Greater resistance to weld overlay disbonding
Benefits for CrMoV steels when applied, calculating example

- outer Diameter: 3.400mm
- overall height: 36.000mm
- design pressure: 170 bar

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<th>design temperature 482 °C</th>
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2007 Edition

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Calculation based on some simplifications

Low alloy CrMo(V) steel plates for petrochemical reactors
Summary of parent material properties

Even for the high plate thickness:

- **12CrMo9-10:**
  The tensile and toughness properties are satisfactory in a HP-range between 19.6 and 20.8

- **CrMoV-steels:**
  In spite the higher tensile requirements HP-values up to 21.1 are acceptable

- **CrMo(V)-steels:**
  Impact toughness increase by tempering effect until an optimum HP value is reached.

- Good toughness reserves even for high HP-values

- **Know-How about mechanical properties in dependence of HP and delivery condition is the basis of the optimum steel design and safe production**
Dillinger experience in processing CrMo(V) steels

- Dillinger Hütte GTS regularly processes CrMo(V) steels in its Heavy Fabrication Division
- the scope of work comprises forming and welding of components for pressure vessels out of CrMo(V) steels, i.e.
  - cold or hot* forming by roll bending or pressing
  - longitudinal welding of shell courses
  - forming of heads in the pressing shop

  (*after hot forming the parts will be heat treated as per the material standard)
Cold forming - Dillinger Hütte’s roll bending machine
Weld edge preparation

Weld edge hardness is mostly restricted by Engineering Spec's e.g. API 934 to max 225BHN for conventionel and 235BHN for advanced steel grades; in some cases to the same level as the base metal.

This can be reached by machining or oxycutting with subsequent grinding.
Milling machine for edge preparation

Possibilities:
- thickness up to 120 mm
- length up to 25000 mm
- width up to 5000 mm
- weight up to 40 t
- extremely tight tolerances
- shape profiling
Edge preparation possibilities

- **X-edge**
- **J-edge**
- **J-X combined edge**
Bend test to check cold forming (cross section 200 x 50 mm) with severe deformation
• no cracks on the machined side even for bending at ambient temperature
• a small crack in the flame cut edge after bending at 170°C
Forming

Cold Forming:
General trend of the influence of cold deformation on mechanical properties
Warm and Hot Forming

Low alloy CrMo(V) steel plates for petrochemical reactors
Mechanical properties of 2.25Cr1MoV-steel in dependence of heat treatments

- Rp0.2 resp. Rm [MPa]
- Av [J], Charpy-V-transv. Top
- Test Temperature -60°C
- Test Temperature -80°C
Torispherical Heads: ID 3500; $s_{\text{min}}$ 180mm, Grade 2.25Cr1Mo (12CrMo9-10)
Plate for torispherical heads ID 3500; $s_{\text{min}}$ 180mm, 12CrMo9-10

heat treatment Q+T+PWHT, initial plate thickness 192mm
Torispherical Heads ID 3500; \( s_{\text{min}} \) 180mm, Steel Grade 2.25Cr1Mo (12CrMo9-10)

head hot formed, Q+T + simulated PWHT

![Graph showing the impact of test temperature on Av [J].](image)

After step cooling

Low alloy CrMo(V) steel plates for petrochemical reactors
Welding - general recommendations

Reactors made out of CrMo(V)-steels are characterized by:

- extreme wall thickness
- strong hardenability
- severe service conditions

precaution and careful processing required

closer look to:

- HAZ hardness
- Delayed HICC
- Toughness in the weld / step cooling

API RP- 934, ASME VIII-2, App. 26
SA 542 D4a

Shell inside

120mm

Shell outside
• Mandatory request for intermediate stress relieving (ISR) application for nozzle welds

• Need for a tight control of preheating and interpass temperature application

• Tight control of PWHT temperature

• Careful attention for temporary attachment and/or attachment welds (e.g. insulation supports)

• Personnel education.
Weld metal and HAZ in the as welded condition are susceptible to hydrogen induced cold cracking.

**How to avoid this defect?**:

- dry and clean weld bevels
- select low hydrogen consumables and treat them properly to minimise hydrogen input (rebaking, storage, heated quivers ...)
- keep the weld at sufficiently high temperatures until the weld is completed (>180°C)
- lower the concentration of residual hydrogen by heat treatment immediately after welding (300-350°C)
- lower the hardness and cracking susceptibility by PWHT (~700°C) or „intermediate PWHT“ (~650-670°C)
Influence of PWHT on toughness charpy-V -20°C for 2.25CrMoV

PWHT 680°C, 5h
- individ. 1(J)
- individ. 2(J)
- individ. 3(J)
- average(J)

PWHT 680°C, 10h
- individ. 1(J)
- individ. 2(J)
- individ. 3(J)
- average(J)
Influence of PWHT on toughness; PWHT 710°C, 30h for 2.25CrMoV

![Graph showing the influence of PWHT on toughness for 2.25CrMoV steel plates. The graph plots the Charpy V-notch energy (J) against temperature (-20°C, -40°C) for different regions: HAZ top, HAZ 1/4, HAZ 1/2, HAZ 3/4, weld metal top, weld metal 1/4, weld metal 1/2, and weld metal 3/4. The average energy is also shown.]}
Influence of PWHT on weld metal and HAZ toughness @ -20°C

2¼CrMoV

Test temperature: -20°C

PWHT 30hrs @ 710 °C
PWHT 10hrs @ 680 °C
PWHT 5hrs @ 680 °C

Low alloy CrMo(V) steel plates for petrochemical reactors
Low alloy CrMo(V) steel plates for petrochemical reactors

Weld metal: Transition curves for different PWHT conditions

Source: Elettrotermochimica S.r.l.
Figure 7 – Charpy V-Notch Toughness of Vanadium Modified 2¼Cr-1Mo Deposited Weld Metal after ISR Using a Second Alternative Wire Flux Combination (16)
Weld metal: Transition curves for different PWHT conditions

| Heat treat Condition | As welded | ISR 650°C / 5 hrs. | ISR 670°C / 2 hrs. | ISR 670°C / 5 hrs. | ISR 690°C / 2 hrs. | ISR 690°C / 5 hrs. | ISR 650°C / 5 hr. | ISR 705°C / 10hrs. |
|---------------------|----------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|---------------------|-------------------|
| Impacts (Joules at 0°C) | 9, 7, 8 | 13, 6, 8           | 14, 9, 15          | 21, 23, 71         | 65, 80, 119        | 80, 147, 82        | 80, 147, 82        | 216, 205, 203      |

Table 2 – Mechanical Properties of Vanadium Modified Sub-Arc Weld Metal as Function of PWHT Conditions (ISR) \(^{(17)}\)
PWHT-limits to be destined according to ASME VIII, App. 26

- 680°C, 5 hours
- 680°C, 10 hours
- 710°C, 30 hours

FIG. 26-300.1
All Weld Metal Tensile Test

- Rm: 585 - 760 N/mm²
- Re: ≥ 415 N/mm²

PWHT 705°C, 30hrs
PWHT 705°C, 8hrs

Low alloy CrMo(V) steel plates for petrochemical reactors
Impact Test Charpy-V, PWHT 705°C, 30hrs

The diagram shows the impact test results for low alloy CrMo(V) steel plates after post-weld heat treatment (PWHT) at 705°C for 30 hours. The chart plots the average energy (Av) in Joules (J) against different regions and temperatures:

- Weld Metal (WM) -18°C
- HAZ -18°C
- WM -45°C
- HAZ -45°C

The data is represented by individual points and their averages, categorized by location (Top, Center, 3/4 T). Each category has different markers for individual tests (1, 2, 3) and a common symbol for the average.
Influence of step-cooling test, PWHT: 705 °C/8 hrs; Location: HAZ center

Test Criteria:
\[ T_{Tr} + \text{Faktor} \times \Delta T_{Tr} \leq \text{max. shift} \]

<table>
<thead>
<tr>
<th>Order-No</th>
<th>674739</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref.-No</td>
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<tr>
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<td>55470</td>
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<td>Material</td>
<td>SA 542-D-4a</td>
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<tr>
<td>Thickness</td>
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<tr>
<td>HP:</td>
<td>Weld seam: X</td>
</tr>
<tr>
<td></td>
<td>Current: AC</td>
</tr>
<tr>
<td></td>
<td>Position: HAZ center</td>
</tr>
</tbody>
</table>

Faktor: 2.5
max. Shift 10 °C
Min Av 54 J

\[ T_{Tr}, \text{without Step-Cooling: } -99,15 \, ^\circ C \]
\[ T_{Tr, SC}, \text{with Step-Cooling: } -80,40 \, ^\circ C \]
\[ DT_{Tr} = T_{Tr, SC} - T_{Tr} = 18,75 \, ^\circ C \]

Test criteria fulfilled: Yes
Influence of Step-Cooling, PWHT: 705 °C/ 8hrs; Location: Weld metal center

Test Criteria:
$T_{Tr} + \text{Faktor} \times \Delta T_{Tr} \leq \text{max. shift}$

Faktor: 2.5
max. Shift | 10 °C
Min Av | 54 J
$T_{Tr}$ without Step-Cooling: -61.19 °C
$T_{Tr}$ with Step-Cooling: -64.84 °C
$DT_{Tr} = T_{Tr}^{sc} - T_{Tr} | -3.65 °C$
test criteria fulfilled | Yes
Influence of Step-cooling on the transition temperature

![Graph showing the influence of step-cooling on the transition temperature. The graph plots $T_{T54J}$ before Step Cooling against $T_{T54J}$ after Step Cooling. Below the straight line $T_{T54J} + 2.5 \times \Delta T \leq 10 ^\circ C$, some points are marked as not fulfilled, while others are marked as fulfilled. The legend includes symbols for base material 2.25CrMoV, weld metal 2.25CrMoV, HAZ 2.25CrMoV, base material 3CrMoV, weld metal 3CrMoV, and HAZ 3CrMoV.]
HAZ hardness comparison of CrMo- and CrMoV-steel

- **650°C-10h**: 2¼CrMo¼V as welded
- **675°C-10h**: 2¼CrMo¼V as welded
- **700°C-10h**: 2¼CrMo¼V as welded
- **725°C-10h**: 2¼CrMo¼V as welded

**Hardness [HV10]**
- **235**
- **250**
- **400**

**Cooling time t_{8/5}**
HAZ hardness vs. cooling time $t_{8/5}$ and PWHT (bead on plate)

- 2.25CrMoV as welded
- 2.25CrMoV 705 °C / 10 h
- 2.25CrMoV 705 °C / 30 h
- 3CrMoV as welded
- 3CrMoV 705 °C / 10 h
- 3CrMoV 705 °C / 30 h
- 12CrMo9-10 as welded
- 12CrMo9-10 690 °C / 10 h
- 12CrMo9-10 690 °C / 30 h

Cooling times:
- TIG: ca. 3-5 sec
- GTAW: 3-12 sec
- SMAW: 5-20 sec
- SAW: 10-40 sec
- Electro Slag: > 50 sec
Influence of PWHT on Vickers-hardness of the welded joint for 2.25CrMoV

PWHT 705°C, 30hrs
PWHT 705°C, 8hrs
Influence of PWHT on Brinell-hardness for 2.25CrMoV

PWHT 705°C, 8hrs
PWHT 705°C, 30hrs

Low alloy CrMo(V) steel plates for petrochemical reactors 83
Development of carbides during PWHT

**As welded**
no carbides

**620°C - 15’**
M$_3$C few M$_{23}$C$_6$

**730°C - 8h**
M$_7$C$_3$, M$_{23}$C$_6$,
fine V$_4$C$_3$, M$_2$C

TEM micrographs on carbon extraction replica 2$^{1/4}$CrMoV

Ref.: Lundin, C.D. and K.K. Khan, WRC Bulletin 409

Low alloy CrMo(V) steel plates for petrochemical reactors
Disadvantages of Vanadium modified steels

• No cost advantage over conventional steel even though lighter vessels.
• Greater sensitivity to weld cracking during fabrication.
• ISR mandatory for highly stressed joints e.g. nozzles, bed supports, etc.
• Higher PWHT temperature required.
• Field weld repairs more difficult.
• Weld materials not readily available (limited suppliers)
• Low toughness of "as welded" weld deposit prior to PWHT.
• Higher deposited weld metal hardness
• Successful fabrication requires experience and tight control of production parameters (narrow production window)
  
  => E.g. cracking problems from rolling of welded plate have been reported
Creep properties

• German code (AD-Merkblatt) allows an extrapolation of creep results to a factor of only 3
  ⇒ necessity to provide the creep resistance for at least 30,000 h if a vessel is designed for 10 years, even 70,000 h for expected 20 years in service. This criterion will also be used in the future for the European Standard EN 13445 for Unfired Pressure Vessel.

• In case of reactor design in creep regime: if creep strength values on welded joints are verified to be within a 20%-scatter band of the base material
  ⇒ welding consumable and base metal from the material manufacturer duly approved by tests within the creep regime can be used for fully stressed welds using a joint efficiency factor of 1 instead of 0.8 (design according to German AD-Merkblatt, in future also according to EN 13445)
Heat affected zone hardness

- Welds of CrMo(V) reactors steels are always subjected to PWHT
- Coarse grained heat affected zone (CG-HAZ) is usually the area of highest hardness within the HAZ
- The main “tempering effect” is obtained by intensive PWHT
- The essential parameter to control HAZ hardness are time and temperature of PWHT
Benefits of Vanadium addition in regard to creep behaviour

- Vanadium carbides provide increased creep rupture life to chrome moly alloys.
- Vanadium addition enhances creep rupture life of 2 ½Cr alloys to a degree greater than that for 3Cr & 5Cr alloys.

Source JSW
Creep test results CrMo(V) steels (base metal) at 500°C
Conclusion

- CrMo steels with ¼ % V offer improved performance for petrochemical reactors compared to enhanced 2¼Cr1Mo steels. Plates are commercially available up to about 250 mm thickness.

- Welding needs precautions, in particular: tight control of preheat, interpass temperature intermediate stress relieving and post weld heating to avoid cold cracking.

- Optimized welding consumables have to be used with respect to low hydrogen input and very low impurity level to limit in service embrittlement.

- Screening tests of the weld metal before production starts, e.g. as per API RP 934, are recommended.

- The steels tolerate very high temperatures 690 - 710 °C for post weld heat treatment, which is beneficial for the toughness of the weld metal.

- DH-GTS is a long term supplier with plenty of know how for high sophisticated steels.

- A wide range of dimensions can be supplied.

- More and more vessels will be designed from CrMoV steels to take advantage of improved process possibilities and improved properties.