HEAVY PLATE FOR PETROCHEMICAL REACTORS

SOPHISTICATION IN CHROMIUM-MOLYBDENUM STEEL

DILLINGER HÜTTE GTS

EXPERIENCE THAT MASTERS EVEN THE GREATEST DEMANDS

Construction of reactors and vessels for the petrochemicals industry makes enormous demands on the steels used. Low-alloy chromium-molybdenum steels (1 to 3 % Cr and 0.5 to 1 % Mo) are normally selected for the fabrication of heat exchangers and process reactors. Vessels for elevated high-pressure hydrogen-resistance specifications, as in the case of hydrotreaters, hydrodesulfurizers and hydrocrackers, for example, are constructed from plate with increasingly more sophisticated specifications. Dillinger Hütte GTS has a well established worldwide reputation as a dependable partner for petrochemicals reactor engineering, not only because our plate meets the very highest standards, but also because adherence to delivery agreements, an increasingly important factor in a globalized world, is among the top priorities at Dillinger Hütte GTS.

Decades of experience, exceptional technological potentials, and cooperation with designers, users and operators have enabled Dillinger Hütte GTS to play its own special role in the development and use of Cr-Mo steels for high-pressure hydrogen-resistant reactors. In many of the world's refineries, engineers rely on reactors fabricated from Dillingen steels, with their excellent properties and mastery of even the most demanding specifications. Development of ever higher-performance and more efficient reactors operated at higher temperatures and pressures continues without interruption, confronting steelmakers and their products with ever new challenges. Dillinger Hütte GTS has also built up a valuable store of experience in the context of research projects conducted with operators and material users in the further development and refinement of traditional materials into the range of vanadium-modified steels. The ultra-modern steels resulting from these projects, and permitting significant reduction in vessel weights, are already in use in numerous reactors around the globe. Dillinger Hütte GTS has been able to supply these steels, which are now included in the most commonly used codes and standards, for this growing market for a number of years now.

Pressure vessel out of SA 387-22-2 [1]

[1] *courtesy of Larsen & Toubro Ltd.*

[2] *courtesy of Kobe Steel Ltd., Energy Systems Division*

585 t pressure vessel out of SA 542-D-4A for a refinery project [2]

THE BENEFITS OF CR-MO PLATE FROM DILLINGEN IN MORE DETAIL

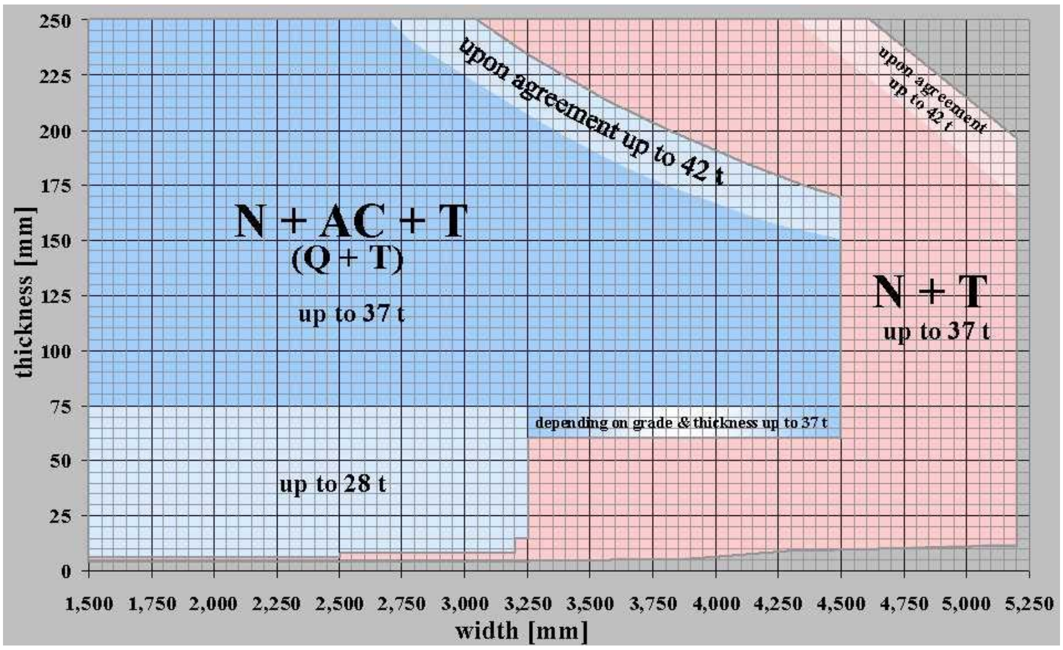
Dillinger Hütte GTS uses one of the world's most efficient and capable rolling lines for its plate production. This mill makes it possible to enter dimensional ranges otherwise scarcely accessible, such as net widths of up to 5,200 mm, for example. Even greater widths are possible on agreement for round blanks. The powerful four high stands enable, for example, to achieve high toughness values in thick plates, even at the center. To realize this the High-Shape-Factor-Rolling is applied. The high-performance drive systems installed in the rolling stands permit high per rolling pass reduction rates, achieving total deformation of the center zone of the plate at an early stage of rolling. These benefits enable the reactor manufacturer to use lower-cost heavy plate as an alternative to forgings for high wall thicknesses.

Out-of-the-ordinary plate formats reduce the scope of welding, permit forming of large-diameter seamless vessel heads, and provide designers with more freedom. Other benefits include enhanced component safety and cost reductions deriving from reduced scopes of production and inspection.

CrMo grades according to delivery program

type of composition	acc. to ASTM/ASME	acc. to EN 10028-2, 2003
1Cr ½Mo	A/SA387-12-Cl 1/2	13CrMo4-5
1¼Cr ½Mo	A/SA387-11-Cl. 1/2	13CrMoSi5-5
2¼Cr 1Mo	A/SA387-22-Cl.1/2 A/SA542-A/B-3/4/4a	10CrMo9-10 12CrMo9-10
2¼Cr 1Mo ¼V	A/SA832-22V A/SA542-D-4/4a	13CrMoV9-10
3Cr 1Mo ¼V	A/SA832-23V A/SA542-E-4/4a	12CrMoV12-10

Dillinger Hütte GTS can supply Cr-Mo steels in conformity with the most commonly used standards, such as ASTM / ASME and EN 10028, Part 2. Customers normally specify numerous requirements exceeding those in the relevant standard. These can reliably be met by Dillinger Hütte GTS.

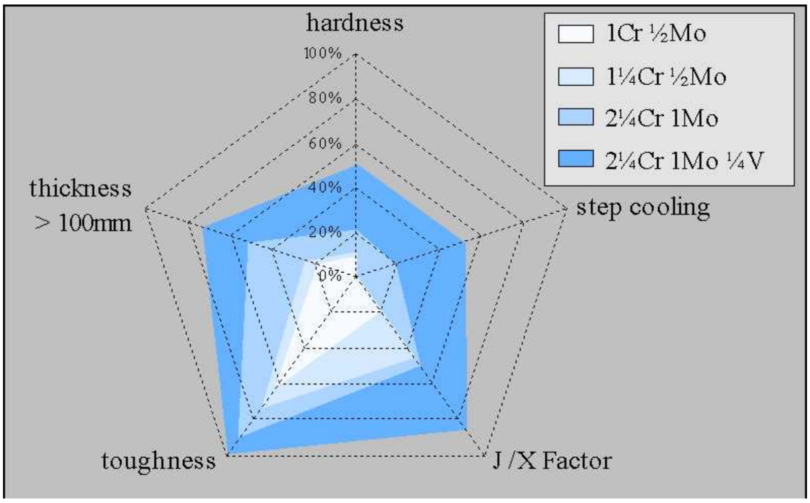


Potential dimensions for CrMo steels as a function of delivery condition. The flatness specifications for plate widths from 4,500 mm upward must be separately agreed; widths from 5,100 mm upward can be supplied only in unflattened state. The maximum plate thickness in N+T condition is often limited by the specification.

COOPERATION – THE KEY TO THE DESIRED PROPERTY PROFILE

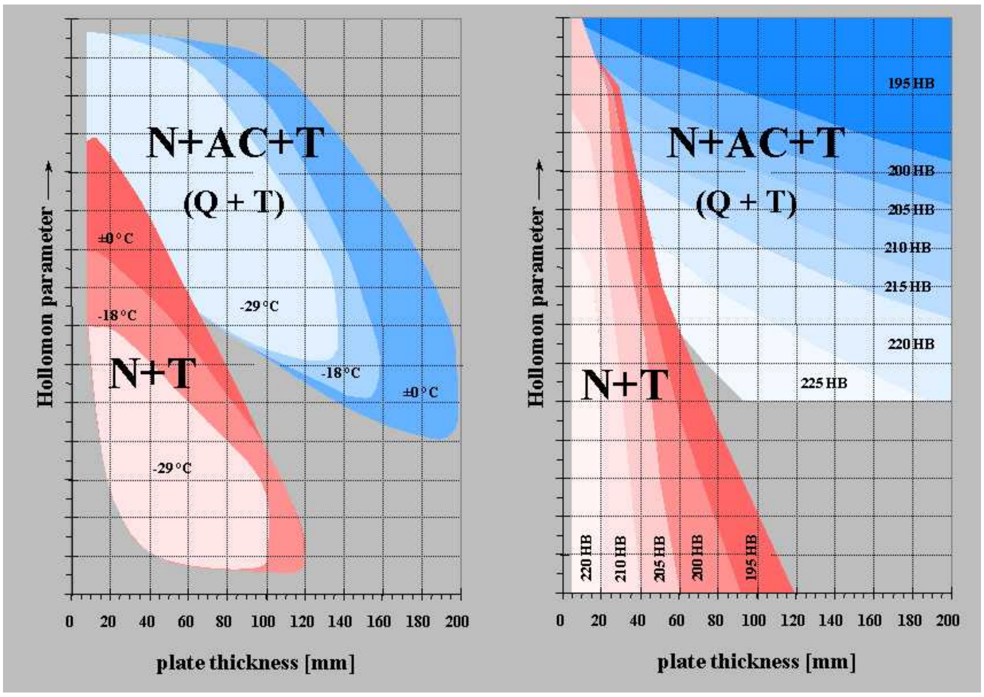
Petrochemical process reactors are designed to cope safely with the longest possible campaign times under exposure to high pressures, high temperatures and attack by pressurized hydrogen. The relevant codes and standards specify the essential orientational data for steelwork design; mechanical and technological data, such as yield strength at room temperature, at elevated temperature and in the creep range, for example. The necessary impact energy and the ranking in the Nelson diagram are also stipulated.
It should be noted that it is not only chemical composition and plate thickness which influence materials properties.
Heat-treatment conditions (normalizing, tempering, water quenching and tempering, and stress-relieving annealing) and, where appropriate, hot forming during further processing and working, all play a decisive role. In addition, the material properties in the long term service can change also after manufacturing of the pressure vessels.

In consultation with plate users, designers and plant operators, Dillinger Hütte GTS takes these influencing factors into account in its steel design from the very start, in order to supply a steel which optimally fulfils the property specification. A differentiated and individual requirement profile will result and must be fulfilled, orientated around the steel type involved, for every application.



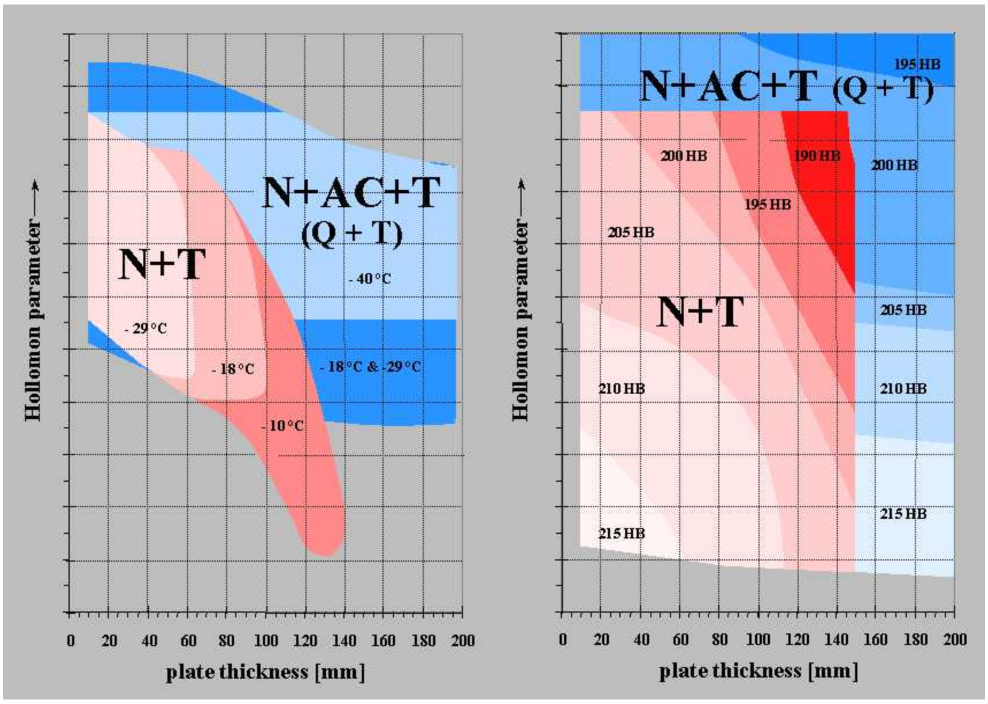
Frequency of enquiry concerning certain central properties and enquiry parameters for various CrMo grades.

Investigations performed by Dillinger Hütte GTS using the example of tempering and stress-relieving annealing of air quenched and tempered Cr-Mo steels, and water quenched and tempered Cr-Mo steels, illustrate the way different heat treatments can affect technological feasibility. Temperature and residence time during heat treatment are summarized in so-called Hollomon parameters to permit easily comprehensible illustration of the correlations involved.
It is apparent that, where stress-relieving annealing requirements are high (equating to high Hollomon parameters), only water quenched and tempered Cr-Mo steels are capable of meeting the necessary strength and toughness specifications.



Impact energy *Brinell hardness*

SA 387-11-2 *(1¼Cr ½Mo)*



Impact energy *Brinell hardness*

SA 387-22-2 (2¼Cr 1Mo)

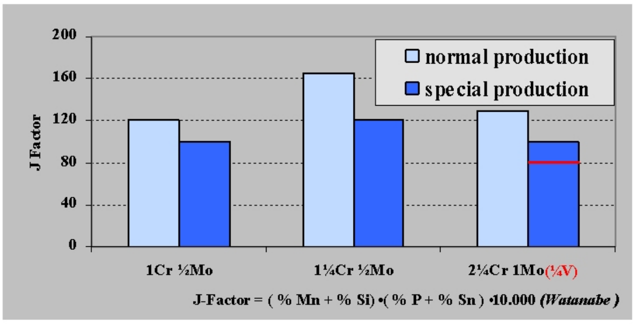
Examples of the influence of complex requirements in terms of feasibility, using the example of a 1¼Cr ½Mo steel (SA 387-11-2) and a 2¼Cr 1Mo steel (SA 387-22-2).

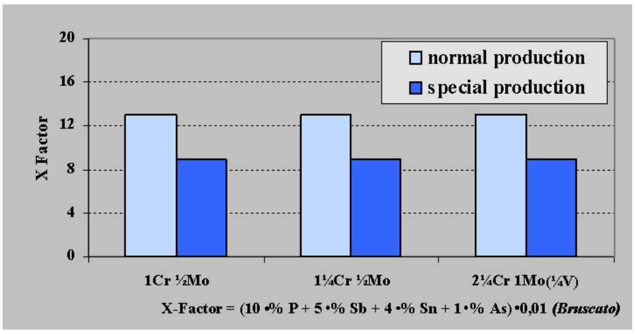
The way in which agreeability limits vary as a function of delivery condition and Hollomon parameters (heat treatment and plate thickness) is illustrated for a composition type. A specified minimum yield strength of $R_{p0.2} \geq 311$ *MPa and a specified minimum tensile strength of* $518 \leq R_m \leq 689$ *MPa form the basis for these diagrams. The toughness level for the various test temperatures for the individual zones is an average of 31 Joule.*

HIGH TOUGHNESS LEVELS
EVEN IN LONG-TERM SERVICE

The fact that creep-resistant Cr-Mo steels have a tendency to long-term embrittlement has been known for more than half a century. This occurs, typically, in the approx. 370° C to 580° C temperature range. A characteristic feature of such long-term embrittlement is a shift in impact energy transition temperature toward higher values. This phenomenon is attributed in the relevant literature to the influence of the trace elements P, Sb, As and Sn in the steel.

Various empirical correlations based on the chemical analysis are used for estimation of the proneness to embrittlement of various steels. The best known are the J or Watanabe factor, and the X or Bruscato factor developed for deposited weld material. Since Dillinger Hütte GTS produces its steel solely on the basis of "virgin" ore, using the blast furnace/oxygen top-blowing converter route, the trace element contents of its products are extremely small. The results are extremely low J and X factor values.





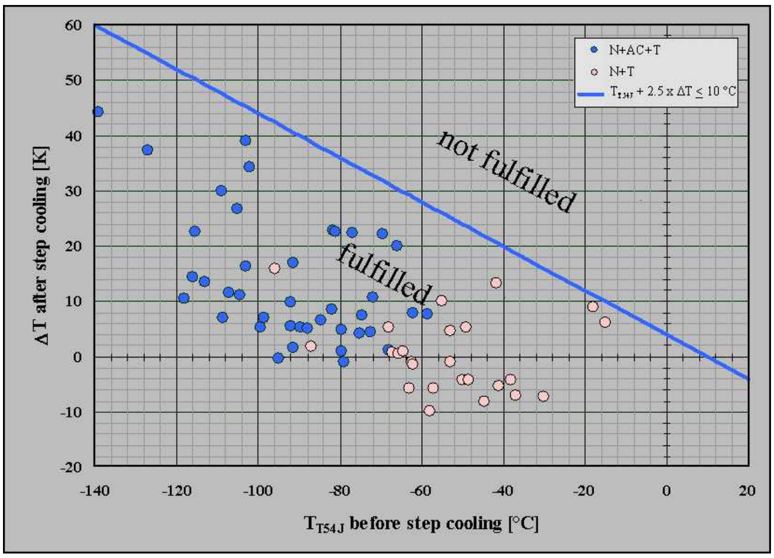
Agreeable values for the J and X factors

	normal production	special production
P	**0.011 %**	**0.006 resp. 0.007 %***
Sn	**0.005 %**	**0.005 %**
As	**0.007 %**	**0.007 %**
Sb	**0.001 %**	**0.001 %**

* depending on Cr-content

Maximum trace element contents

Tests performed by Dillinger Hütte GTS have demonstrated that, at such low trace element contents, proneness to embrittlement does not necessarily correlate with the J and X factor, or with P content. So-called Step Cooling makes it possible to assess the sensitivity of a steel to embrittlement. The shift in impact energy transition temperature, measured after Step Cooling, multiplied by a factor (normally 2.5) corresponds on the basis of present-day knowledge to the shift which occurs after many years of service. Dillinger Hütte GTS therefore recommends inclusion of the Step Cooling Test in the order for the steel.



Quantification of sensitivity to embrittlement: Shift in impact energy transition temperature after Step Cooling as a function of delivery state and transition temperature prior to Step Cooling. All points located below the straight line represent pairs of values which meet the requirements.

DILLINGER HÜTTE GTS
- MORE FROM PLATE

In fabrication of reactors, the plate used must undergo a whole series of frequently complex working operations. At this stage, many fabricators can reach the limits of their technological potentials, particularly where thick large format plate is involved. Dillinger Hütte GTS does not leave its customers to cope on their own in such cases. The Heavy Fabrication Division in Dillingen, with its extensive range of equipment and machines and its experience in processing of out-of-the-ordinary plate formats, can offer such companies and fabricators an "extended workbench" when their own possibilities are exhausted. For many years Dillinger Hütte GTS has been supplying semi-finished or partly prefabricated components to customers world-wide, such as:

One-piece heads and pressings: Spherical heads with outer diameters of up to 3.650 mm, torispherical and elliptical heads of up to 4.450 mm and flat heads of up to 4.750 mm can be produced from one plate, up to a maximum plate thickness of 200 mm, depending on the steel grade; they can also be delivered in water quenched and tempered condition. Multi-segment heads consisting of ready-to-assemble segments can be supplied for even larger diameters.

Longitudinally welded shell-courses: Shell courses of thicknesses up to 300 mm and 4.300 mm lengths can be cold bent, depending on the steel grade. We can also perform hot forming and the heat treatments necessary after forming.

Edge-machined plates: Plates with prepared welding edges in a 5 to 120 mm thickness range can be produced using an ultra-modern edge-milling machine.

Plate cutting: The Heavy Fabrication Division uses NC coordinate-guided thermal cutting machines to cut plate of up to 350 mm thickness to size and shape with high precision in accordance with customers' specifications and design drawings.

Components can be supplied in conformity with the relevant codes and standards, such as DGRL 97/23/EC, EN 13445, ASME, AD2000, PD5500, etc., for example. Approval marks, such as ASME Stamps S, U and U2 are available. Further information on these capabilities is given in the "Delivery Program Heavy Fabrication Division Dillinger Hütte GTS".

Cold bending of a 240 mm thick shell section in the Heavy Fabrication Division shop.

WE MAKE THE STEEL

Please contact our sales organizations if you would like to request a quotation from Dillinger Hütte GTS. Further information on materials is available via our service telephone: +49 (0)6831 47 34 53.

Sales organizations:

Germany
Vertriebsgesellschaft
Dillinger Hütte GTS
Postfach 104927
70043 Stuttgart
Tel.: +49 711 61 46 300
Fax.: +49 711 61 46 221

France
Dilling-GTS Ventes
5, rue Luigi Cherubini
93212 la Plaine Saint Denis Cédex
Tel: +33 1 71 92 16 74
Fax: +33 1 71 92 17 98

Other countries

Please contact our coordination office in Dillingen, or visit our Internet site, to obtain contact with your local representative:
www.dillinger.de

Tel.: +49 6831 47 23 85
Fax.: +49 6831 47 99 24 72

AG der Dillinger Hüttenwerke
Postfach 1580
66748 Dillingen/Saar

e-mail: info@dillinger.biz
http://www.dillinger.de

Tel.: +49 6831 47-34 53
Fax.: +49 6831 47-99 3450

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