DILLINGER offshore LETTER

CrMo steel plates for petrochemical reactors

An improved performance of hydrocarbon processing plants can be achieved by using higher working temperatures and pressures. This development means new challenges and applications for our plates. With these targets in mind, 2.25Cr1Mo steels are used today especially for the construction of petrochemical reactors such as hydrocracking, hydrotreating or desulphurizing reactors. Crude oil cracking processes are performed at temperatures of between 400-460 °C (752-860 °F) and under total pressures of between 20 to 185 bar with hydrogen partial pressures of between 5 and 150 bar! For hydrogen conversion reactors the design conditions are even more severe.

In the past few years, hydrocarbon processing plants have called for bigger and heavier reactors. Thus, plate demand has shifted not only towards greater thicknesses due to an increase in pressure but also towards greater widths and lengths. In some cases new types of CrMo steels such as the enhanced type A542Cl.4 or the vanadium modified types of 3Cr1Mo and the 2.25Cr1Mo steels are used mainly for hydrocrackers.

DILLINGER HÜTTE GTS is able to supply a great variety of CrMo steel grades, as can be seen from Table 1; Table 2 gives our maximum plate dimensions depending on delivery conditions. The table shows that plate widths of up to 5,200 mm can be produced at Dillingen, this being of particular interest for the forming of "one piece heads" which can be manufactured by our Heavy Fabrication Division (see Table 3).

TABLE 1: Survey of CrMo qualities produced by DH GTS

Standard	Steel quality
EN 10 028-2	13CrMo4-5
	10CrMo9-10
	11CrMo9-10
VdTÜV data sheet 404/1	12CrMo9-10
NF A 36-206	10CD9 10
ASTM/ASME	A/SA387Gr11Cl1/2
	A/SA387Gr12Cl1/2
	A/SA387Gr21Cl1/2
	A/SA387Gr22Cl1/2
ASTM/ASME	A542 Type B Cl4

TABLE 2: DH GTS delivery possibilities - dimensions (plates)

Delivery condition	max. width (mm)	max. thickness (mm)	max. unit weight (t)
as rolled	5,200 *)	≈ 200 **)	36
N+T	5,200 ***)	≈ 200 **)	36
Q+T	4,500	≈ 200 **)	36

*) plates with rolled mill edge in widths of up to 5,400 mm, e.g. for large one-piece circular blank/heads or circular tube sheets (on inquiry)

**) max. thickness mainly limited by specification requirements

***) for lengths > 18 m, max. width = 4,300 mm

TABLE 3: DH GTS delivery possibilities - dimensions (heads/shells)

elliptical heads	max. Ø OD = 4,400 mm
hemispherical heads	max. Ø OD = 3,400 mm
max. wall thickness heads	≈ 200 mm
shells	≈ 220 mm

As mentioned above, reactors for hydrocarbon processing or vessels made of CrMo steel plates are operated at a temperature range of about 400-480 °C (772-896 °F) and it is well known that in this range embrittlement of the steels may occur. An embrittlement of the material over time entails the risk of brittle fracture, especially when the vessels are set up or shut down. For this reason it is absolutely necessary to maintain a minimum material impact capacity at about room temperature, even after several years.

It is believed that embrittlement is mainly caused by elements such as Sb, Sn, P and As, since these elements have the tendency to diffuse to the grain boundaries and precipitate at temperatures of between 300 and 500 °C (572 and 932 °F). Other elements such as Mn and Si are thought to activate this phenomenon.

In order to describe the tendency for embrittlement of CrMo steels, Watanabe proposed using the so-called J-factor that he had developed on the basis of his own experience:

$$J = (Mn\% + Si\%) \times (P\% + Sn\%) \times 10\,000$$

In the material specifications of the various companies max. values for J of 200, 150 or even 100 are usually required. Besides the J-factor another embrittlement parameter, the so-called X-factor or Bruscato-factor, is sometimes specified:

$$X = (10P + 5Sb + 4Sn + As) : 100$$
(all in ppm)

This factor was originally developed for filler material in butt welds. Nevertheless, it is often used for the base material, too. Table 4 shows the lowest J and X-factors for the various CrMo qualities which can be offered by DILLINGER HÜTTE GTS. These extremely low factors can easily be achieved in Dillingen because the base for the pig iron, which is converted to steel in a basic oxygen converter (BOF), is iron ore containing extremely low quantities of As, Sn and Sb. In contrast to this the base for the electric (E-) furnace route is scrap which often contains harmful residual elements.

As the possibilities of achieving very low P contents in the steel are the same for both the BOF and E-furnace, Table 5 gives a comparative overview of the contents of As, Sn, Sb and P achievable in CrMo steels for the BOF and E-furnace production- route.

It is well known that embrittlement in service can be simulated in the laboratory by the so- called "step cooling test". The shift of a Ch-V-transition curve at 55 J before and after the step cooling test is used to measure the embrittlement. The in-service embrittlement corresponds, according to an API study, with the ΔT 55 J shift of the step cooling test multiplied by a factor of 2.5 to 3.

The above-mentioned embrittlement factors J and X, as well as other factors, e.g. those developed by the MPC (Materials Properties Council), aimed to avoid the time-consuming and expensive step cooling test. In Figure 1 the ΔT 55 J shifts for 2.25Cr1Mo steels measured by Watanabe and values of 2.25Cr1Mo and 1Cr0.5Mo heats of DILLINGER HÜTTE GTS are plotted over their J-values. As can be seen there exists only a very poor correlation with which to predict ΔT 55 J by given J-factors.

TABLE 4: Optimum offer from DILLINGER HÜTTE GTS for J and X-factors

Grade	J-factor	X-factor	Remark
13CrMo4-5	≤ 70	7 ppm	–
A387Gr11	≤ 100	7 ppm	Si ≥ 0.50 %
A387Gr12	≤ 80	9 ppm	Si ≤ 0.40 %
A387Gr22	≤ 80	9 ppm	Si ≤ 0.50 %
10CrMo9-10	≤ 80	9 ppm	–
12CrMo9-10	≤ 80	9 ppm	–

TABLE 5: Possibilities of DH GTS BOF process and other steel processes

Heat analyses (%)	DH GTS (BOF)	Others (E-furnace)
Sn	≤ 0.002	≤ 0.003/0.010 ***)
P	≤ 0.005 *)/0.013 **)	≤ 0.005/0.010 ***)
As	≤ 0.004	≤ 0.005/0.015 ***)
Sb	≤ 0.001	≤ 0.002/0.005 ***)
Total	≤ 0.012/0.020 **)	≤ 0.015/0.040 ***)

*) P content due to special treatment
**) normal P content
***) with/without scrap selection

FIGURE 1: Influence of J-factor on T_{55J} - transition temperature shift after step cooling

$\Delta T_{55J} = T_{55J}$ (after S.C.) – T_{55J} (before S.C.)

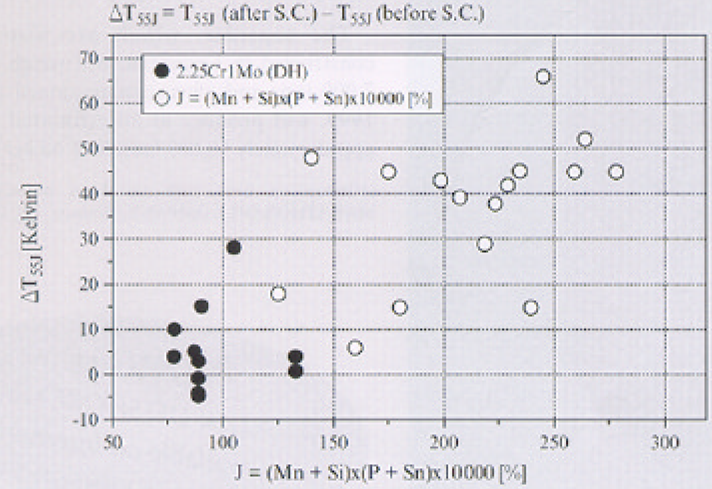
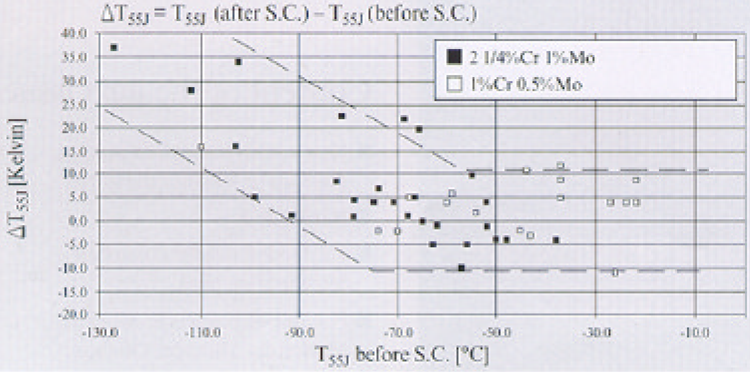


FIGURE 2: Influence of T_{55J} - transition temperature before step cooling on ΔT_{55J} - shift

$\Delta T_{55J} = T_{55J}$ (after S.C.) – T_{55J} (before S.C.)



The ΔT 55 J results at Dillingen of -10 to +20 K (with the exception of 5 results) show no correlation with the J-values. A similar behaviour was found when the Dillingen ΔT 55 J-shift results had been plotted over the X-factor or over the other proposed factors, e.g. (P+Sn), or the factors developed by the MPC. The only tendency we have found is that ΔT 55 J depends on the temperature of 55 Joule before the step cooling test as can be seen from Figure 2.

These results give us an indication of the direction we will take in our research to discover which parameters will really influence the embrittlement behavior of CrMo steels. Another field to which DH GTS is committed is the development of V-modified 2 1/4Cr1Mo and 3Cr1Mo qualities as we see great advantages for these steels in comparison to the conventional 2 1/4Cr1Mo steel.

Up to now we have tested and welded several heavy plates from industrial heats with thicknesses of up to 200 mm in each of the V-modified qualities, some with excellent results. We will continue our research in various fields, on the one hand to help find the answers to some questions which are still open and, on the other, to be able to satisfy the demands of our customers.

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Publications

- Brochure "HEAVY FABRICATION DIVISION - Delivery program"
- Folder "REFINEMENT FROM CHROMIUM MOLYBDENUM STEEL - Heavy plate for petrochemical reactor construction"
- Folder "DICREST - Plates with homogeneous HIC-resistance"

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