Welding and Properties of the New 2¼Cr and 3Cr1Mo¼V Steels For Hydrocrackers

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INTRODUCTION

The evolution of Cr-Mo steels for the petrochemical industry has been driven, in the last ten to twenty years, by increasing process severity (increase of temperature, increase of hydrogen pressure) setting, in turn, new requirements for the materials, and by the new possibilities of the steel making process.

For design temperatures up to **454°C**, the possibility to use "enhanced" 2¼ **Cr 1 Mo** was given to the constructors by the **ASME** Code Case 1960 in December 1984. However, the conditions expected for synthetic fuel processes may lead to increase in the design temperature up to 482°C (ref. 1). For such applications, materials with additions of Vanadium to improve the creep and hydrogen attack resistance have been investigated in **API/MPC** (American Petroleum Institute/ Material Properties Council) research programmes. In a previous work performed on laboratory heats, Creusot-Loire Industrie demonstrated that high resistance to hydrogen damages may be expected from these family of V modified steel grades (ref. 2). These observations were confirmed on industrial products of thickness 150 mm to 300 mm (ref. 3).

As a consequence of **API/MPC** research work, two new steel grades have been introduced in the **ASME** code :

- In December 1984, the **3 Cr 1 Mo¼ V Ti B** steel grade in the Code Case 1961.
- In August 1990, the **2¼ Cr 1 Mo¼ V** steel grade in the Code Case 2098.

This paper will present the development of special welding products able to reach equivalent mechanical properties of the base material : strength, creep and toughness taking into consideration the **P**ost **W**eld **H**eat Treatment **(PWHT)** conditions, the "disbonding" phenomenon of the austenitic cladding made by the **SAW** and **RES** is discussed.

FILLER METALS

For the construction of hydrocrackers using **3 Cr 1 Mo** 0.25 **V** and **2¼ Cr 1 Mo** 0.25 **V** steels as specified in the already mentioned Code Case 1961-1 and 2098-1, suitable filler metal for the arc welding processes SAW and SMAW must be available, which match the requirements for the specified mechanical properties of the steels and the welding behaviour under shop conditions.

In comparison to the standard grade **2¼ Cr 1 Mo** type these steels contain additional elements such as V, Nb and Ti.

Developing filler metals for these steels, the question has to be answered, which of these elements are necessary in the weld metal and what concentration guarantees adequate creep resistance and toughness properties after step cooling. Alloying elements having a favourable influence on the mechanical properties of the steel, do not however have such an influence on the weld metal.

Inspite of this knowledge, in the first stage of development parts of a plate have been forged into ingots, which have then been hot rolled. The hot rolled wire was then drawn to 4 mm, which was used for SAW and the production of covered electrodes.

Having experience with the deteriorating influence of vanadium and niobium on the toughness properties, at first it seems nearly impossible to get the required toughness level of 54J at – 20°C before and after step cooling.

Based on the results of the investigation of this melt and the experience, which were available from the development and production of filler metals for the standard and advanced **2¼ Cr 1 Mo** type, further test melts with an optimized chemical composition have been investigated.

In the first stage the standard post weld heat treatment of 20h at 690°C usually applied for **2¼ Cr 1 Mo** weld metal has been chosen. **PWHT**'s at higher temperatures up to 710°C improve the toughness properties at low temperatures and time decreases the hardness. In this case the question has to be answered upto which temperature and time the specified mechanical properties of the steel as for instance **YS, UTS** and **HTS** are matched in the weld metal and in the steel after **PWHT**.

The analysis of filler metals for welding **2¼ Cr 1 Mo** 0.25 **V** steel are specified in Code Case 2098-1 (Table 1). Nb and V which increase the heat and creep resistance, have at the same time a deteriorating influence on the toughnes properties at low temperatures. An important task in the development was to reduce these elements to the lowest possible limit, by balancing them with other elements.

In code Case 1961-1 only the analysis of **Cr 1 Mo** 0.25 **V** steel is specified. Upto now there is no specification in this Code for the weld metal.

Based on the Code Case 2098-1 for **2¼ 3 Cr 1 Mo** 0.25 **V** weld metal the filler metals for welding 3 Cr 1 Mo 0.25 V steel has been alloyed with V and Nb for improving the creep properties.

Welding of 3 Cr 1 Mo 0,25 V steel

SMAW

For optimizing the mechanical properties, covered electrodes have been developed with and without Nb in the coating. Already the low addition of Nb decreases the toughness level at low temperatures significantly. The question was, if it is possible to compensate this negative effect by changing the **PWHT**, for the creep test without Nb in the weld metal, showed that the measured values were below the limits for the steel (Fig 1).The results of different **PWHT**'s are shown in Fig 2. The impact-temperature curves are translated with longer time to lower temperatures. The similar effect can be observed after step cooling, Fig 3. The same

Table 1 : Chemical composition of weld metals for welding CrMoV-steels

	C	Si	Mn	P	S	Mo	Cr	V	Nb	As	Sb	Sn
SMAW Chromo 3 V	0,09	0,17	0,63	0,011	0,006	1,09	2,97	0,25	0,012	0,003	0,006	0,002
SAW CrMo3V - 430 TTR-W weld metal	0,12	0,14	0,70	0,009	0,004	1,04	3,01	0,25	0,016	0,006	≤ 0,001	0,004
Requirement acc. Code Case 2098-1 weld metal min.	0,08	0,10	0,60			0,90	2,25	0,25	0,010			
max.	0,15	0,30	1,10	0,015	0,010	1,10	2,60	0,38	0,025			
SMAW Chromo 2V	0,09	0,14	0,64	0,009	0,007	1,10	2,27	0,26	0,016	0,003	≤ 0,001	0,005
SAW CrMo2V - 430 TTR-W weld metal	0,09	0,16	0,65	0,009	0,002	1,00	2,48	0,28	0,012	0,004	≤ 0,001	0,003

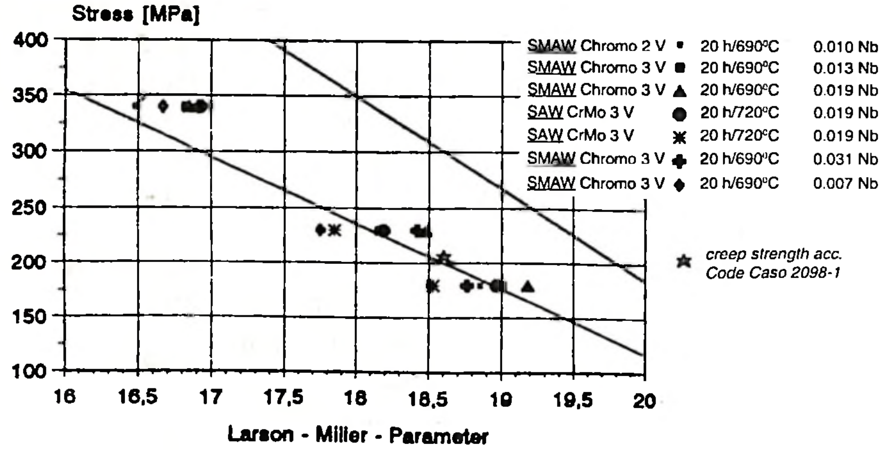

Fig. 1 : Creep Properties of CrMoV Weld Metal

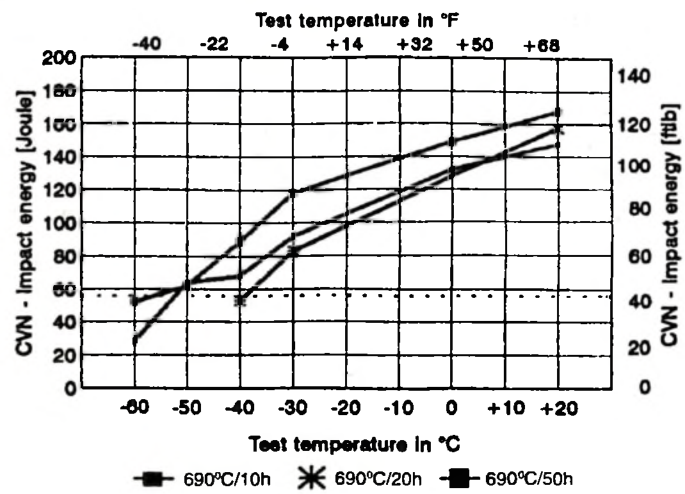

Fig. 2 : Toughness Properties Of 3 Cr-1 Mo-0, 25 V Weld Metal (SMAW)

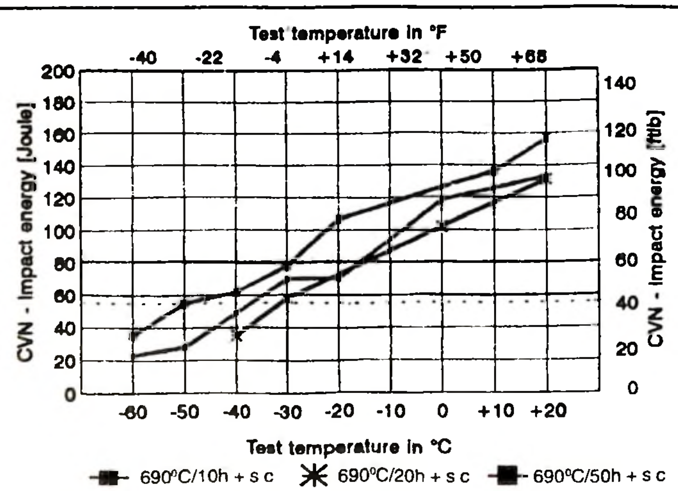

Fig. 3 : Toughness Properties of 3 Cr-1 Mo-0, 25 V Weld Metal (SMAW)

behaviour can be achieved by increasing the pwht temperature, which is shown later. When drawing these results into a Larson Miller (tempering parameter) diagram, the toughness properties may be estimated at other **PWHT**'s (Fig 4).

The result of tensile tests are plotted in the L.M. diagram (Fig 5) and an estimation can be made for min. and max time for the **PWHT** matching the mechanical properties of the steel.

With regard to the toughness and the UTS the heat treatment for the weld metal should be 10 to 30h at 705°C. This lower and upper limit has been used for an additional investigation to verify the theoretical estimation.

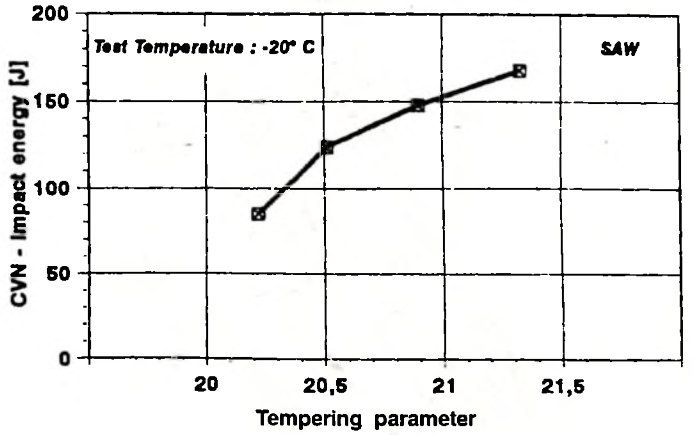

Fig. 4 : Influence of T.P. on the Toughness Properties (3 Cr-1 Mo-0, 25 V Weld Metal)

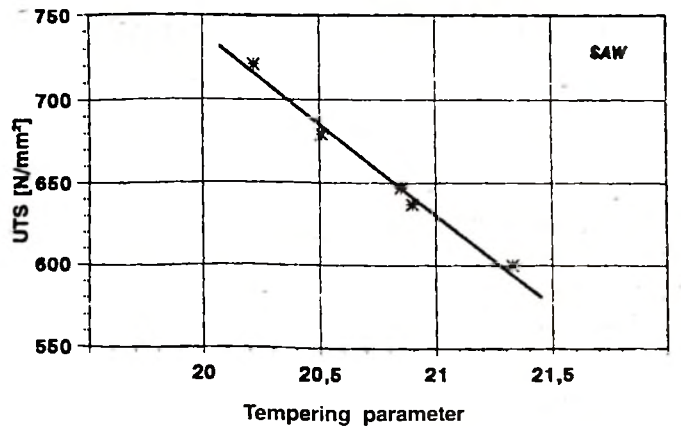

Fig. 5 : Influence of T.P. on Tensile Strength (3 Cr-1 Mo-0, 25 V Weld Metal)

SAW

Investigations with the wire S 1 CrMo 3 V and the standard flux for welding 2¼ Cr 1 Mo steel has shown, that the toughness requirement of 54J (40 ft-lbs) at -20°C could not be matched. Therefore the new fluorid basic flux 430 TTR-W has been developed. The influence of Niobium as well as the different heat treatment conditions including step cooling remain the same as it had been described for the weld deposit of covered electrodes.

Welding of 2¼ Cr 1 Mo 0.25 V Steel

SMAW AND SAW

Based on the experiences with welding of 3 Cr 1 Mo 0,25 V steel filler metals for the above mentioned steel for SMAW and SAW have been developed. The experimental heat has been used for the production of the SAW wire as well as for producing stick electrodes. The required toughness properties of the Code Case 2098-1 are match for SAW and SMAW weld metal after a heat treatment of 20h at 690°C. The influence of the Nb-content on the toughness is the same as for 3Cr 1 Mo 0,25 V weld metal.

Investigations of the mechanical properties are running after 10h at 705°C and 30h at 705°C. We think that these **PWHT**'s will lead to optimized results in view of the mechanical properties, toughness

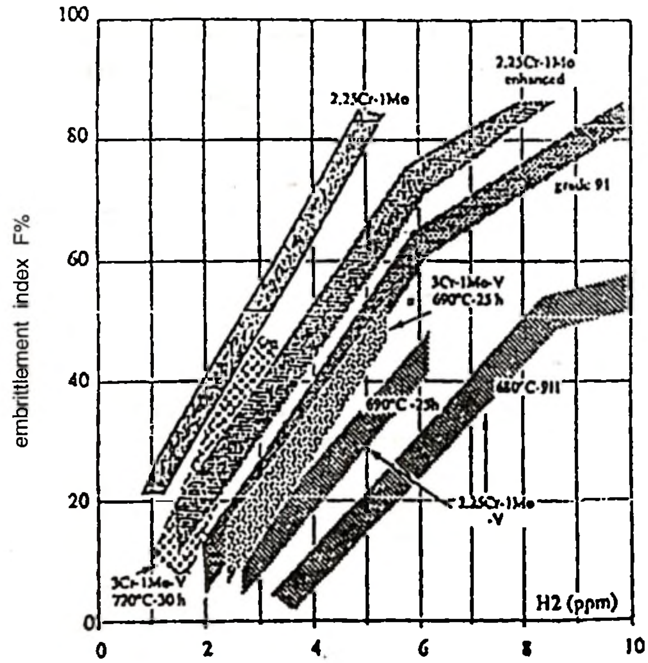

Fig. 6 : Results of F % Hydrogen Embrittlement Tests

level at - 18°C and sufficient creep properties in the weldment. For test welding an industrial heat of 30 t weight has been used. Creep tests are running and will be presented as soon as they are available.

Hydrogen embrittlement

To evaluate the sensitivity of hydrogen embrittlement, the charging conditions are chosen more close to the operating conditions. In fact, in that type of test, the objective is to introduce a controlled quantity of hydrogen on the specimen and to test it quickly to measure the direct effect of hydrogen content on the steel ductility or toughness.

Typical charging conditions were selected as follows :

- In autoclave under 150 bar H_2 at 450°C for a few days.
- Cathodic charging in an acidic solution (HCl/H_2SO_4).
- H_2S charging in saturated NACE solution.

This permitted to cover range of hydrogen content from 1 to 10 ppm. The figure 6 shows the ductility loss (noted here F %) versus the hydrogen content measured on the specimen just after testing.

DL (Ductility Loss %)
$$= [(RA_{UC} - RA_{HC})/RA_{UC}] \times 100$$

(RA : Reduction of Area, UC : Uncharged, HC : Hydrogen Charged)

All new materials appear to have an improved resistance to hydrogen embrittlement compared with the reference standard 2¼ Cr 1 Mo steel grade. Also PWHT is shown to be an important parameter. Considering the ductility loss for an hydrogen content of 3/4 ppm, which is the quantity expected to be present in the material after shut down, it is clear that materials offer higher embrittlement resistance than the standard materials (see table 5). The test performed on full well metal of 3 Cr 1 Mo V Nb shows higher embrittlement resistance for that material. This behaviour is commonly observed for weld material. It is attributed to the trapping effect of numerous and homogeneously distributed micro non-metallic spheric inclusions on hydrogen atoms. So a small quantity of hydrogen is trapped on each particle reducing the local embrittling effect.

DISBONDING

Disbonding phenomenon is due to the conjuntion of both hydrogen oversaturation and the presence of sensitive microstructure at the interface between the stainless steel overlay and the base material (ref. 4-5-6).

Hydrogen concentration at the interface results from the solubility and the diffusivity of this element in the cladding and in the base material in the temperature range from room to operating temperature [482°C (900°F)].

From this point of view, the 2¼ and 3 Cr 1 Mo¼ V steel grade

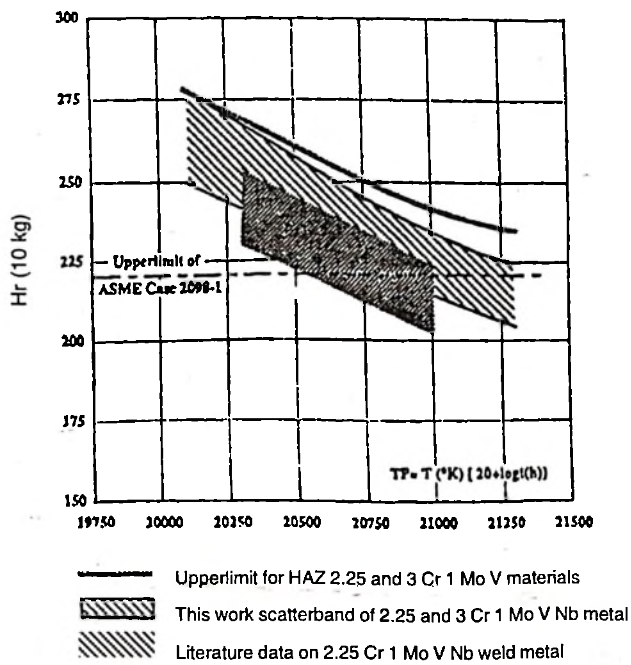

Fig. 7 : Evolution of Hardness in HAZ and Welds of 2¼ Cr and 3 Cr 1 Mo V Steels

offer an improvement compared to the standard 2¼ Cr 1 Mo steel. Calculations of the hydrogen peak at the interface made by Brouwer (ref. 7) for similar operating and the shut down sequences show that the new 3 Cr 1 Mo ¼ V Steel will reduce the hydrogen peak intensity by about ten times.

The presence of a sensitive microstructure at the interface is more difficult to evaluate. It has been proved that both cladding and base material chemistries are concerned.

Many parameters have to be considered :

- the weld overlay chemistry results from strip and flux qualities, dilution of the base material, and welding parameters;
- the weld and interface microstructure also result from the above mentioned parameters.
- the carburization of the interface area results from the carbon gradient between the weld overlay and the base material, the carbide's stability and the PWHT conditions.

The best way to evaluate the disbonding resistance is to perform high severity tests which consist in hydrogen charging of representative specimens and then cool down quickly to maximise the hydrogen peak to the interface of the cladding. Then ultrasonic detection is practiced on the specimen to measure the percentage of disbonded interface.

Such type of tests have been performed on a lot of situations concerning weld overlays and 2¼ or 3 Cr 1 Mo ¼ V steel grades as following. The disbonding test specimens (ref. 3) were charged at 482°C (900°F) under a pressure of 150 bars. The time of exposure was 40 hours followed by evacuation of hydrogen, opening of the autoclave and cooling of the specimen at 675°C/h (1250°F/h) (ref. 8). Although very tough conditions have been used on the specimens described in this page, no disbonding has been observed.

DISCUSSION ON OPTIMIZING PWHT

It has been shown above that the Tempering Parameter (**TP**) resulting from the **PWHT** temperature and time is of major importance for a lot of properties of base and weld materials. Considering first the basic mechanical properties (tensile strength and Charrpy V impact energy) it has been observed that increasing the **TP** reduces the strength and improve the Charpy values.

This strength reduction is critical for base material (2¼ or 3 Cr 1 Mo V) for TP values above 21,300 and charpy data of weld metal may be too low for TP values lower than 20,300. In addition, considering the creep properties of base and weld materials it has been observed that the upper limit of TP must be reduced to about 21,000.

So, the optimized PWHT condition appears to be such that TP values are in the range 20,500 to 21,000. The holding time depends on the thickness as recommended by the codes. For a typical holding time of 10 hours corresponding to very thick material (i.e. 250 mm), and with the opportunity to repeat 3 times the PWHT (total time 30 hours) the best temperature is 705°C.

Considering now the effect of PWHT conditions on the hydrogen resistance of these materials, we have to examine the different mechanisms of hydrogen damage:

- The disbonding resistance of stainless steel overlay interface with Cr Mo steels is generally reduced when increasing the TP, because the recarburization of the interface from base material is increased. However, the severe test practiced in the TP range from 20,500 to 21,000 have never given any disbonding effect (ref. 3).
- The hydrogen attack resistance is at the opposite, reduced when decreasing the TP because of the lower stability of carbides. However it has been observed that, even for a TP value of 20,000, the resistance to hydrogen attack is much higher than that of the standard 2¼ Cr 1 Mo steel grade.
- The hydrogen embrittlement resistance decreases when TP value increases, due probably to the reduction of the trapping effect when numerous small carbides are progressively replaced by bigger ones. Tests performed for TP values up to 21,300 have shown that the hydrogen resistance of these materials remains higher than that of standard 2¼ Cr 1 Mo steel grade.

So, considering the global resistance to hydrogen damage, the optimal TP resulting for mechanical properties (20,500 to 21,000), is totally convenient to give a very high resistance to these materials in hydrogen environment.

The situation concerning the hardness properties is not so clear :

- One condition due to the hydrogen embrittlement resistance, derived from the NACE rules for materials operating in **H_2S** environment, is to require a maximum hardness of 22 HRC (equivalent to ~/- 250 HV) at any place of the vessel (includig HAZ of welds).
- Another one concerns particularly the weld metal deposit in the ASME Code Case 2098-1 for which a maximum bardness of 205 HB (equivalent to ~/- 220 HV) is required (Fig. 7)

It is clear that the first requirement may be more or less satisfied for TP values above 20,500. However, the very resistance of these materials to hydrogen damage has been proved even for hardness levels higher than 250 HV and that limit may be discussed.

More important is the fact, that to guarantee a maximum hardness level of 220 HV in the weld metal, the PWHT will be very high (above 21,000 for literature data on 2¼ Cr 1 Mo V and above 21,500 for data resulting from that work). Both conditions are not compatible with the optimized mechanical properties (tensile, Charpy V and creep) of base and welds. We think that the requirement of the ASME Case on this point will be clarified.

CONCLUSIONS

The V-modified CrMo steels have been found of high interest for pressure vessels operating at high temperature and under high hydrogen pressure. In particular, compared with the standard 2,25 Cr 1 Mo steel, these materials offer a high creep resistance and a higher resistance to the hydrogen damages.

The special welding products developed for joining such materials (SMAW and SAW) have reached equivalent properties than those of base materials after a Post Weld Heat Treatment in the optimum range of 20,500 to 21,000 of the Larson and Miller parameter.

Due to the particular operating conditions (high temperature and hydrogen pressure), one can think that the risk to propagate disbonding at the interface of the cladding and base material may be increased when the vessels shut down. The different conditions of cladding tested in this work (electroslag and submerged arc strip cladding in one and two layers) demonstrated a very good behaviour of such materials.

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