PHENOMENOLOGICAL ASSESSMENT OF TEMPER EMBRITTLEMENT AT $2^1/_4$Cr-1Mo STEEL

Zumpano Jr., P[(1)] and Ferreira I.[(2)]
PETROBRAS/ENGENHARIA/SL/SEQUI-SP[(1)] and UNICAMP/FEM/DEMA[(2)]
Rod. Pres. Dutra, km.143, São José dos Campos - SP - Brazil - CEP:12.243-690[(1)] and Rua Mendeleiev, s/n. - Cidade Universitária "Zeferino Vaz"- Caixa Postal 6122 - CEP:13.083-690 - Barão Geraldo – Campinas - SP - Brazil[(2)]
petronio@directnet.com.br[(1)]and itamar@fem.unicamp.br[(2)]

Abstract

Low alloy 2 ¼ Cr-1Mo steel are often used at high temperature applications. This steel may have a great decrease in its toughness if temper embrittlement appears, when exposed to temperatures at the range from 375°C to 575°C for a long time, and it will promote hazard of accident during start up or shut down of petrochemical plants. A phenomenological assessment of fracture toughness, by means of CTOD tests at room temperature, was done in welded joints of this steel, embrittled by "Step Cooling" with and without stress, at different regions of heat affected zone. Control of impurities content in the steel was responsible to avoid the development of temper embrittlement as tests showed. No significant variation on tested regions and treatments $CTOD_m$ results were observed.

HDT Reactor Wall

Some HDT (Hydro Desulfuring Treatment) reactors are nowadays under design or assembling in Brazilian petrochemical industry, besides many others already in use. HDT's wall reactor is constituted of three layers. Fig. 1 shows the sketch of the reactor wall, according to Kessler [1].

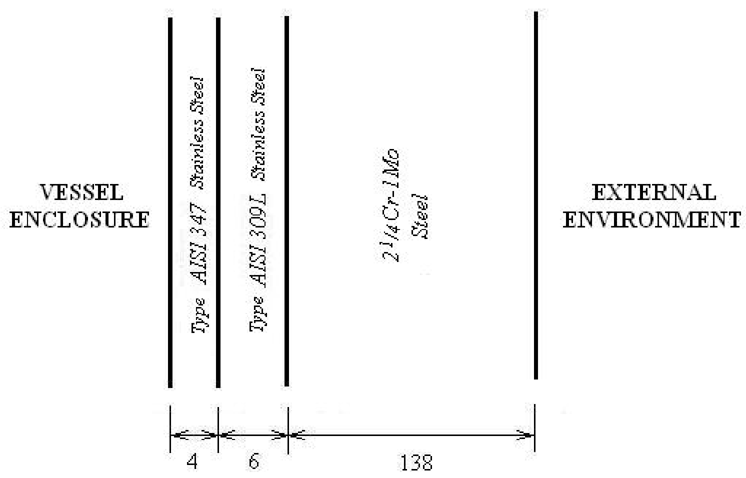


FIGURE 1: Sketch of the HDT wall reactor according to Kessler [1] (dimensions in mm)

The most external layer is a 138 mm plate made with $2^1/_4$Cr-1Mo steel. This is the main plate of the reactor wall, with structural function. There is an internal overlay (“clad”) made by austenitic stainless steel type AISI 347, which protects the vessel from an extremely corrosive environment, containing H_2S at high temperature. An intermediate overlay of austenitic stainless steel type AISI 309L, with thickness of 6 mm, complete the double internal clad. The $2^1/_4$Cr-1Mo steel reactor wall is submitted to a tensile stress of 138,6 MPa, according to Paulo [2], when the reactor is working at its maximum allowable working pressure. Working temperature is 435°C.

The risk of failure increases in situations of shut down and start up of petrochemical units, because of the possibility of embrittlement of $2^1/_4$Cr-1Mo steel after long time and high temperature exposure. Since brittle fracture may occur if a steel is stressed below its transition temperature in the presence of a sufficiently large flaw, hydroprocessing reactors are preheated to a minimum pressurizing temperature (MPT) before been fully pressurized. That temperature is chosen to be safely above the transition temperature for particular steel. HDT reactor stresses are limited to no more than 20 percent of material yield stress, while the reactor steel is below its MPT, greatly reducing the chances of brittle fracture, according to Buscemi [3].

Temper Embrittlement And Step Cooling Simulation

The temper embrittlement phenomenon develops in alloy steels when cooled slowly or isothermally heated in the range of temperature where there is susceptibility to the phenomenon and refers to the progressive loss of toughness at this conditions. Its major consequence is an increase in its tough-brittle transition temperature associated with intergranular failure along prior austenite grain boundaries, according to Hertzberg [4].

It is well established that the fracture toughness of many power plant steels deteriorates during service for two reasons. Firstly, the carbides particles, particularly those located at grain boundaries, coarsen and hence provide easier sites for crack or void nucleation. Secondly, the segregation of impurities to interfaces has an opportunity to proceed to its equilibrium extend during service, according to Bhadeshia [5]. The worst elements for promoting temper embrittlement are: phosphorous, antimony, tin and arsenious. The severity of embrittlement depends not only on the amount of poisonous elements present, but also on the overall chemical composition of the alloy. The interaction of the impurities with the alloy elements may be responsible for the grain boundary segregation and as a consequence for temper embrittlement [4]. Steels are been developed to have low susceptibility to temper embrittlement. Temper embrittlement phenomenon is partially solved by the metallurgical process that guarantee a high control of impurities content of steels, according to Metals Handbook of ASM [7], in the new generation of $2^1/_4$Cr-1Mo steel.

On 60's, General Electric Company developed “Step Cooling" to accelerate temper embrittlement for studying the phenomenon. It consists in submitting the steel to a group of steps of temperatures for certain periods of time, alternated with fixed cooling rates to reduce the temperature of the steps. A sketch of the treatment is showed at Fig. 2. It was suggested by Wignarajah *et al* [6] that "Step Cooling" alone (without something more associated) is not a viable method of estimating long-term embrittlement. On the other hand, Paulo [2], Kessler [1], Teixeira *et al* [8] have gotten important results regarding the validity of “Step Cooling” treatment when associating stress to it.

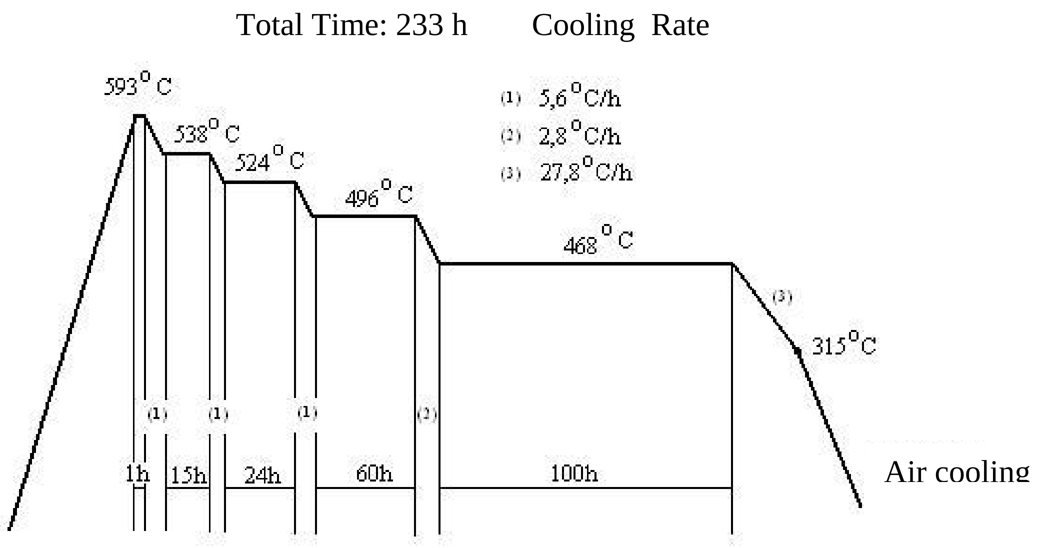


FIGURE 2: Sketch of “Step Cooling” treatment, according to Erwin *et al* [9].

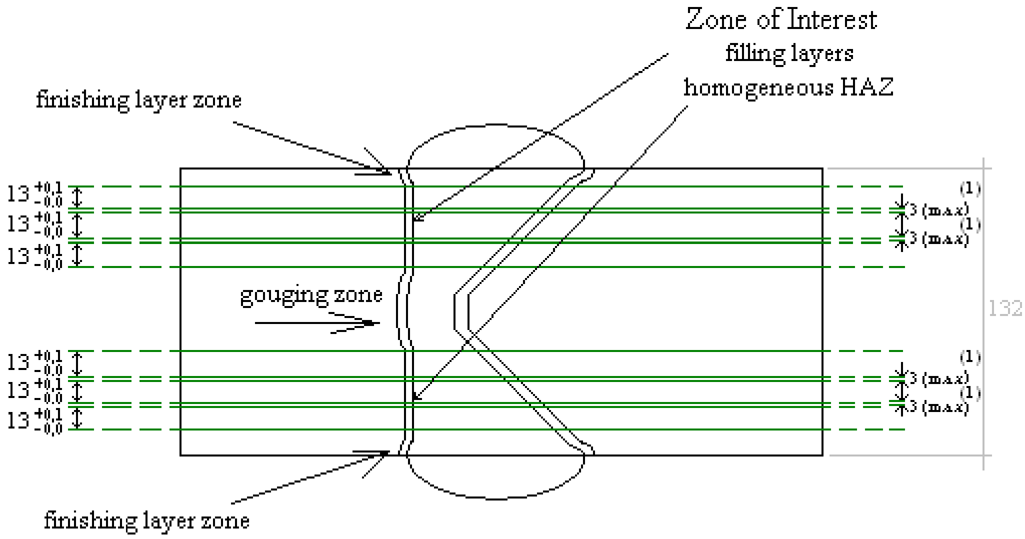
The goal of this work was to analyze fracture toughness, at room temperature, of the heat affected zone (HAZ) of a welded joint of $2^1/_4$Cr-1Mo steel. HAZ was chosen because of being one of the welded joint regions where the lack of toughness can promote the most harmful effects. Room temperature was chosen because of the hazard of accident during start up or shut down of petrochemical plants.

Temper embrittlement assessment is often done by means of Charpy V-notch impact tests due to its lower costs. On the other hand, $CTOD_m$'s tests are much more meaningful regarding crack propagation than Charpy V-notch impact tests. Because of that, fracture toughness parameter analyzed was $CTOD_m$, in welded joints with "K" bevel, at coarse grain (CGHAZ) and fine grain heat affected zone (FGHAZ). According to Anderson [10], for fracture toughness testing (CTOD), in general a through–thickness notch is placed in HAZ's straight side of the “K”. Because of the existent load limits of the equipment gotten to simulate the wall stress of HDT reactors in service conditions while performing “Step Cooling” treatment, the size of CTOD specimens were limited as well. Then, only a phenomenological assessment of the material was made, giving up any goal of getting design parameter regarding HDT reactors, according to Zumpano [11].

Experimental Methods

To get $CTOD_m$ specimens, rectangular sections were machined on welded joints, transversally to the welding progress direction. Bars parallel to the thickness of the plate were taken out from each one of these rectangular sections, as it may be seen at Fig.3. Some bars were submitted to the “Step Cooling” associated with stress, some other bars to the traditional “Step Cooling” and some others remained with no embrittlement simulation. Metallographic analyses were done at the bars to localize the grove and fatigue pre-crack of

CTOD$_m$ specimens on coarse grain heat affected zone (CGHAZ) and fine grain heat affected zone (FGHAZ) of welded joints.



Green lines: Indicated position to take out three upper and three lower bars
(1) The measure indicates the maximum value that may be taken out by saw cut

FIGURE 3: Position to take the bars out from rectangular sections transversally to the welding progress direction, according to Zumpano [11].

After testing, API RP 2Z [12] methodology for verifying the microstructural HAZ region hit by the crack tip was taken. CTOD$_m$ specimens crack surfaces were analyzed at scanning electronic microscope (SEM) to verify fracture mechanisms.

Results And Discussion

Fig. 4 shows the comparison between hardness values of different welded joints regions in each treatment simulation.

The hardness reduction of the specimens after “Step Cooling”, mostly after “Step Cooling” associated with stress may be observed. According to Moss e*t al* [13] and Paulo [2], hardness is an important parameter and may be a first indication for researchers to know if material received the correct thermal treatment. If this initial thermal treatment resulted on carbide precipitation, rich on Mo, so the amount of molybdenum free on solution at ferrite would be lesser and it would increase the amount of free phosphorous and the embrittlement as a consequence. The reduction on hardness levels on “Step Cooled” samples may be explained by means of carbide coarsening at grain boundaries and reduction of carbon inside the matrix.

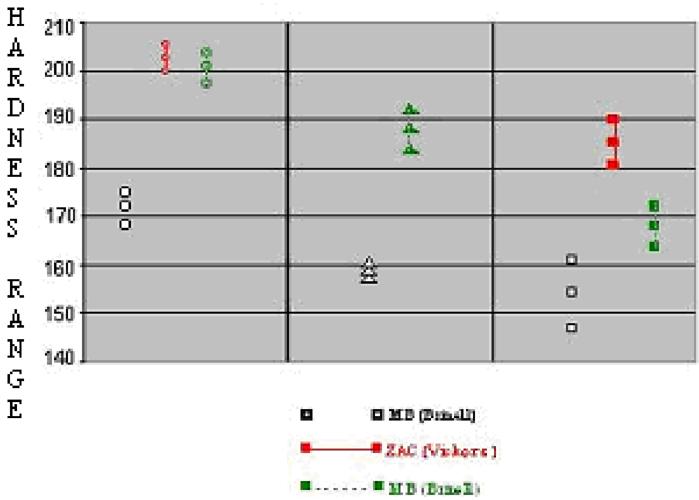
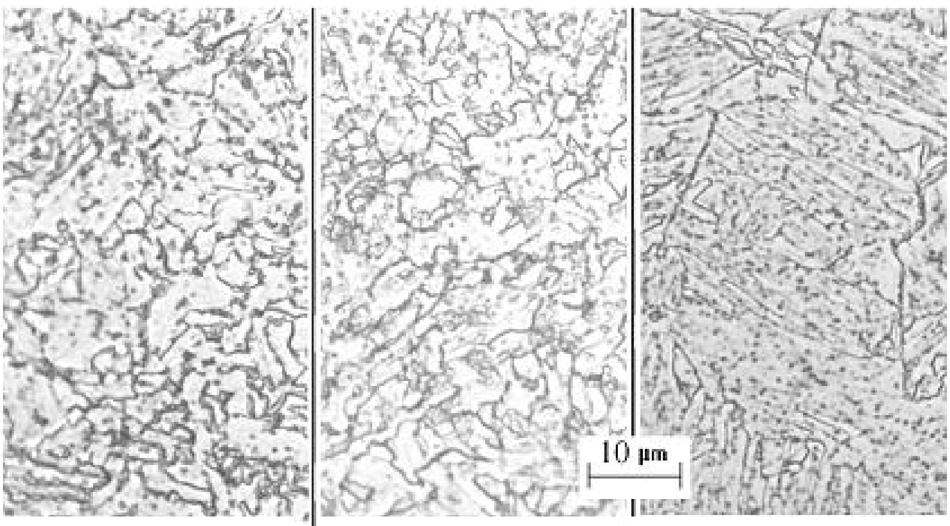


FIGURE 4: Hardness results of different welded joints regions (BM – base metal; HAZ – heat affected zone; WM – weld metal) in each treatment simulation: without Step Cooling (SC), SC without and with stress [11].

At Fig. 5 may be seen, side-by-side, the microstructure of samples at three different treatment conditions. Carbide coarsening may be seen in the grain boundaries and in the matrix at CGHAZ, after "Step Cooling" treatment alone and associated with stress. The same thing may be observed in the samples of other microstructure of weld joint like FGHAZ and Weld Metal.



Sample 1F – CGHAZ
Step Cooling and stress

Sample 6F – CGHAZ
Step Cooling - no stress

Sample 9C – CGHAZ
No Step Cooling

FIGURE 5: Microstructure of CGZAC at three different treatment conditions. Nital 2% - [11].

Carbide precipitation and coalescence in the grain boundaries and in the matrix at CGHAZ and FGHAZ were more intensive after "Step Cooling" associated with stress than after "Step Cooling" treatment alone.

$CTOD_m$ tests results for HAZ at different treatment conditions showed closed values at the three situations, as it may be seen at Fig. 6. No significant differences on fracture toughness values, perceptible on $CTOD_m$ tests, regarding to the different microstructures of HAZ could be observed, as well. The invariance of the fracture toughness values met on HAZ treated by "Step Cooling" alone and associated with stress and on HAZ without "Step Cooling" indicated that the material has reduced susceptibility to temper embrittlement. The invariance on fracture toughness values between CGHAZ and FGHAZ possibly indicated that the welding procedure generated few CGHAZ and much FGHAZ.

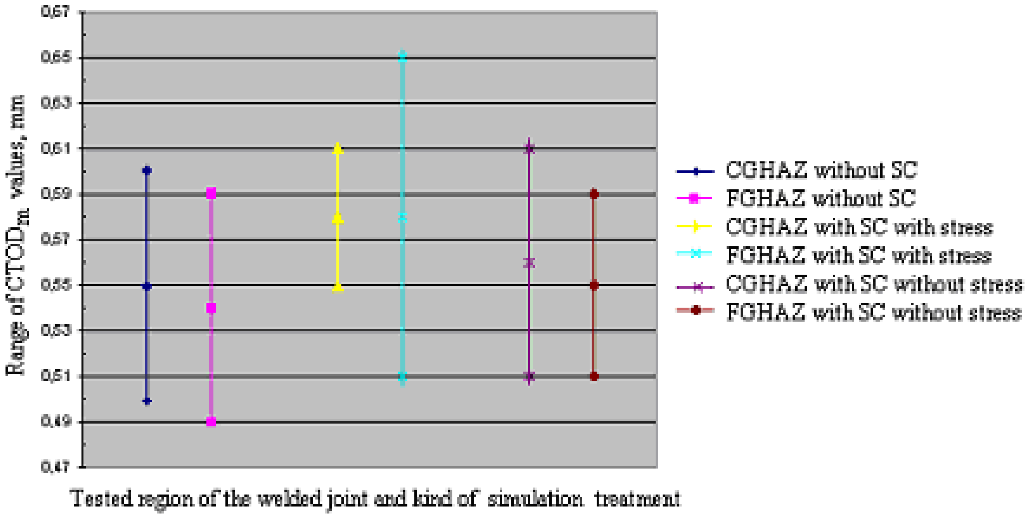


FIGURE 6: Comparison of $CTOD_m$ values (average ± standard deviation) at CGHAZ and at FGHAZ in three treatment conditions (SC = Step Cooling) [11].

Scanning electronic microscope (SEM) fractographs at region of stable crack growth did not reveal significant differences on the fracture mechanism between the three different studied conditions of treatment. Coalescence of micro voids is the predominant mechanism as it may be seen at Fig. 7.

CONCLUSIONS

Hardness reduction at CTOD specimens with Step Cooling may be explained by means of carbon reduction at the matrix caused by carbide precipitation and coalescence at matrix and at grain boundaries, after the embrittlement simulation, what could be proved by the sample microstructural analysis. Step Cooling with stress associated to it showed being more effective on embrittlement simulation. The size of CTOD specimens taken at this work invalidates the results for design parameters to HDT reactors, but it could give a good material behavior analysis, simulating in service conditions of the vessel.

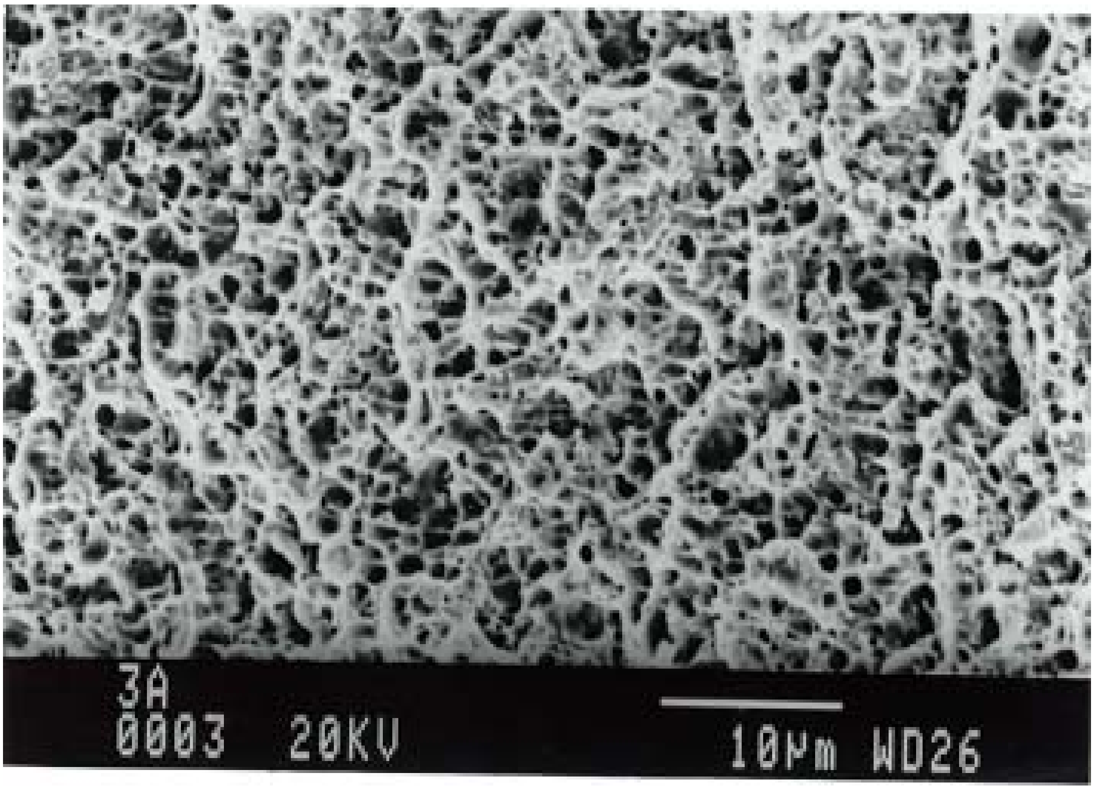


FIGURE 7: Fractography (SEM) of crack surface of $CTOD_m$ specimens, region of stable crack growth (sample 3A) – FGHAZ – with “Step Cooling” + stress [11].

The invariance observed on the fracture toughness values for three different conditions of treatment of the HAZ provides a good indication that this zone of $2^1/_4$Cr-1Mo steel welded joint used on the HDT reactors has small susceptibility to temper embrittlement. The good behavior of $2^1/_4$Cr-1Mo steel welded joint to crack growth, after "Step Cooling”, with and without tensile stress, meets ultimate advances on metallurgy and may be explained by means of the impurities control on the new generation of $2^1/_4$Cr-1Mo steel. It also leads to suggest the possibility of adaptation of the minimum pressurizing temperature (MPT). Microstructural differences between different heat affected zone regions did not implicate in variations at fracture toughness values perceptible by means of $CTOD_m$ tests done and possibly indicated that the welding procedure generated few CGHAZ and much FGHAZ.

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