Fracture Toughness of HAZ in High Temperature Steel for Petrochemical Industry

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Low alloy 2 ¼ Cr-1Mo steel, often used at high temperature applications, when exposed to temperatures at the range from 343°C to 593°C for a long time may be susceptible to temper embrittlement. The risk of failure after temper embrittlement increases in situation of start up or shut down of petrochemical units, when this steel may have a great decrease in its toughness.Fracture toughness (CTODm) at room temperature has been studied, in welded joints of this steel, embrittled by "Step Cooling" with and without tensile stress at coarse grain and fine grain regions of heat affected zone. Experimental results showed that the control of impurities content in the tested steel avoid the development of temper embrittlement. This was confirmed by fracture toughness experiments at room temperature. No significant variation on CTODm results of different tested regions and treatments were observed.

Keywords: high temperature steel, 2¼Cr-1Mo steel, temper embrittlement, fracture toughness

1. Introduction

High temperature steels, which main characteristic is the addition of chromium and molybdenum, are broadly utilized in petroleum and petrochemical industry, particularly in reactors of units that take sulfur out from petroleum derivatives. The HDT (Hydro Desulfuring Treatment) unit reactor chosen to produce this work, even by material supply or by welding procedure specification (WPS) was the reactor projected by PETROBRAS for Refinaria do Planalto (REPLAN) in Campinas. 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 specified according to ASTM A 387 grade 22 class 2. This is the steel of the HDT's reactors wall and it was thermally treated by "Step Cooling" alone and associated with tensile stress, to simulate temper embrittlement in short time period. HAZ was chosen because of being one of the welded joint regions where the lack of toughness can promote the most harmful effects. Metalographic analysis of HAZ and welding metal (WM) in the three different situations of embrittlement was done to verify the effectiveness of "Step Cooling" alone and associated with stress. For the same purpose, hardness tests in the three different welded regions were done: base metal (BM), heat affected zone (HAZ) and welding metal (WM).

HDT's wall reactor is constituted of three layers. Figure 1 shows the sketch of the reactor wall, according to Kessler (2000). 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 and promotes a softer transition between $2^1/_4$Cr-1Mo steel and stainless steel type AISI 347. It absorbs cracks and micro cracks that comes from service pressure, associated to the corrosion of the internal wall, or by the cathodic protection support. Stainless steel type AISI 309L is necessary for having an intermediate thermal expansion coefficient, according to Zumpano (2003). The $2^1/_4$Cr-1Mo steel reactor wall is submitted to a tensile stress of 138,6 MPa, according to Paulo (1998), when the reactor is working at its maximum allowable working pressure. Working temperature is 435°C according to Souza (2001). 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 (1991). The behavior of this steel at room temperature really matters for petroleum and petrochemical industry. The risk of failure increases in situations of shut down and start up of petrochemical units, which have reactors built with this material, because of the $2^1/_4$Cr-1Mo steel embrittlement possibility after long time and high temperature exposure. Accidents that occurred in these conditions are in general related to vessels weld joints, according to Zumpano (2003).

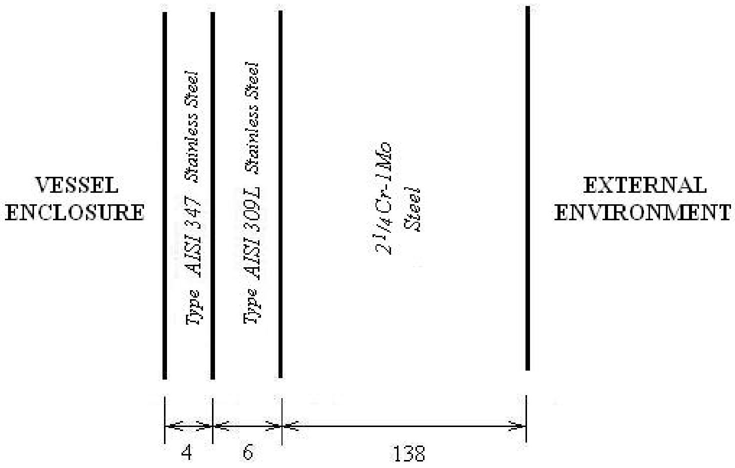


Figure 1: Sketch of the HDT wall reactor according to Kessler (2000) (dimensions in mm).

2. Temper Embrittlement Phenomenon on $2^1/_4$Cr-1Mo Steel and its 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. The major consequence of temper embrittlement is an increase in its tough-brittle transition temperature and it is associated with intergranular failure along prior austenite grain boundaries, according to Hertzberg (1996). The exact range of temperature where there is susceptibility to the phenomenon depends on the steel chemical composition, according to the Metals Handbook of ASM (1975). According to API RP 579 (2000), this range of temperature is from 343°C up to 593°C at $2^1/_4$Cr-1Mo steel. In many cases, the hardness and the strength stress property do not change as a result of temper embrittlement, but the transition temperature may increase up to 100°C for the steel embrittled by thermal treatment, mostly in the old generation of $2^1/_4$Cr-1Mo steel. 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 (2001). The brittle fracture mode becomes increasingly intergranular and occurs at higher and higher temperatures as the segregation level increases, according to Murza (1980). 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, according to Hertzberg (1996). The interaction of the impurities with the alloy elements may be responsible for the grain boundary segregation and as a consequence for temper embrittlement. It was demonstrated that temper embrittlement only occurs on commercial purity steels and it does not occur on high-purity steels, according to Hertzberg (1996). Steels are been developed to have low susceptibility to temper embrittlement. Nowadays, the 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 (1975). Developed on 60's by General Eletric Company in their studies of temper embrittlement of Ni-Cr-Mo turbine rotor steels, the goal of “Step Cooling" was 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. Each pair temperature step / cooling rate produces a different possible carbide in $2^1/_4$Cr-1Mo steel. GE Step Cooling was modified by lengthening exposure time at lower temperatures to allow more embrittlement to occur, according to Erwin et all (1982). Figure 2 shows the sketch of the "Step Cooling" treatment. Wignarajah et all (1990) suggested that phosphorous segregation is a relatively short-term phenomenon, which can be well simulated by G. E. Step Cooling, whereas carbide coarsening behavior, with cannot be well simulated by "Step Cooling", becomes the more dominant cause of embrittlement when considering service periods of 10 or 20 years. Thus, it was suggested by Wignarajah et all (1990) that "Step Cooling" alone (without something more associated) is not a viable method of estimating long-term embrittlement.

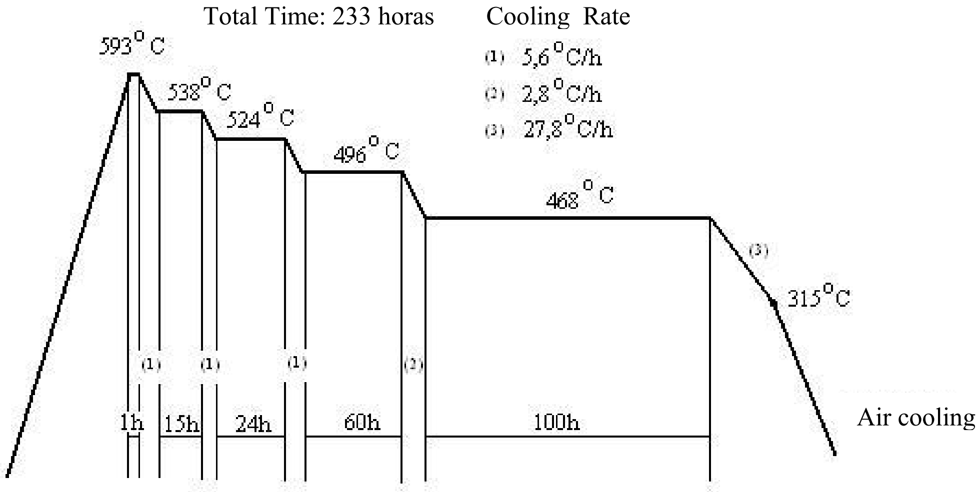


Figure 2: Sketch of "Step Cooling" treatment, according to Erwin et all (1982).

On the other hand, Paulo (1998), Kessler (2000), Teixeira et all (1996) have gotten important results regarding the validity of "Step Cooling" treatment when associating stress to it. According to Kessler (2000), the stress applied on the in service or in the simulating condition, promotes the carbide growth by the strain effect. Kessler (2000) concluded that traditional "Step Cooling" (without stress associated to it) does not have time enough to the carbide coalescence. However, when there is stress associated to it, mostly at the highest stress (138,6 MPa), the presence of carbides increases. The grain boundaries and the matrix manifest an intensive precipitation, according to Kessler (2000). Teixeira et all (1996) studied the effects of the stress on the effectiveness of "Step Cooling" treatment in weld metal (WM) of $2^1/_4$Cr-1Mo steel. They concluded that traditional "Step Cooling" seems not to make a good simulation of embrittlement conditions, although a reduction on impact test energy had been seen. When stress was associated to "Step Cooling" treatment, it promoted a substantial additional reduction on impact test energy, associated with the change on fracture micro-mechanism from transgranular to intergranular (not observed on the traditional "Step Cooling"), characteristic of temper embrittlement phenomenon. Tests were done at -30°C and 0°C. In other work, Paulo (1998) studied the effects of isothermal embrittlement treatments on 468°C and 500°C and "Step Cooling", with and without stress associated to them. He concluded that specimens submitted to thermal treatment with the stress of 138,6 MPa associated to them showed lower hardness values and the strongest level of carbides precipitation, coalescence and growth. Paulo (1998) concluded that stress may have induced carbides precipitation and coalescence, which promoted the reduction on hardness values.

3. Experimental Methods

The welded joint was designed to make HAZ testing easier, according to Anderson (1994). Figure 3 illustrates the preparation in "K" and "half K" preparations. For fracture toughness testing (CTOD), a through–thickness notch is placed in HAZ's straight side of the "K" or "half K" of the CTOD specimens, as shown in figure 3. This work used "K" preparation. British standard BSI 7448:part 2:1997 provides the notch location nomenclature and denote the possible directions to take CTOD specimens out, regarding welding orientation. At this nomenclature N is the direction normal to welding progress, P is the direction parallel to welding progress and Q is weld thickness direction. At this nomenclature the first letter means the direction that is normal to the crack plane and the second letter means the direction of the crack growth.

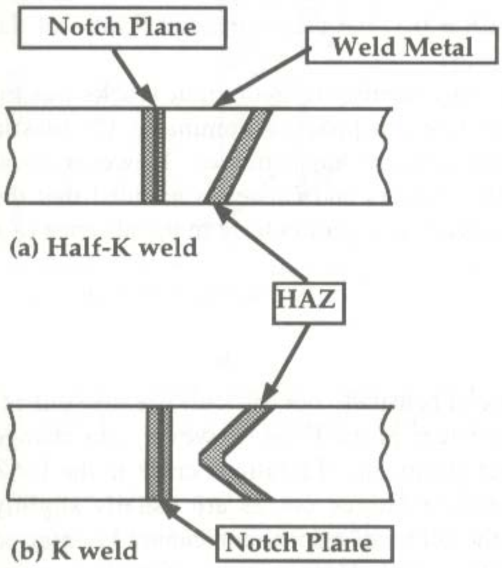
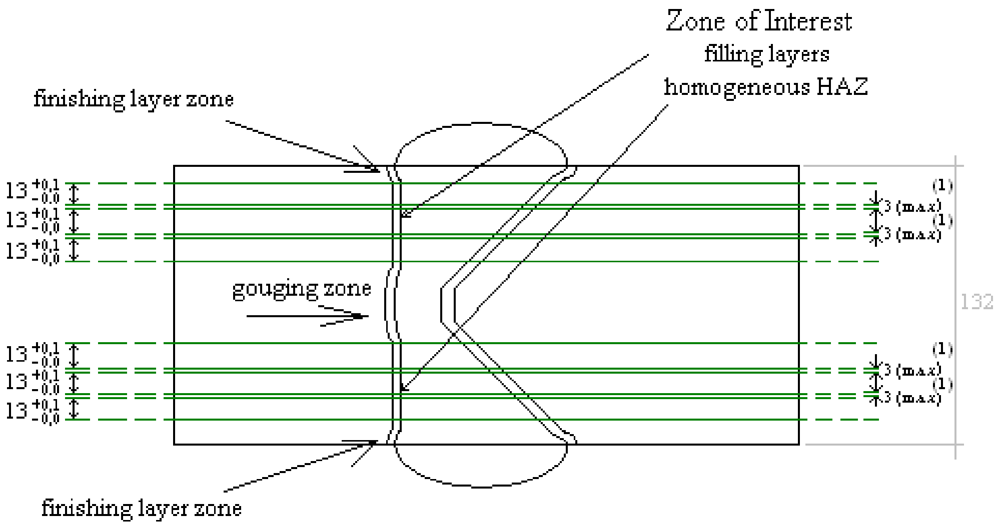


Figure 3: Special designs of welded joints for HAZ fracture toughness tests, according to Anderson (1994).

A big spread of HAZ CTOD results may be observed, mostly in thicker specimens because of the microstructural differences in front of the fatigue pre-crack of the CTOD specimen. Because of this, the methodology shown at the API recommended practice API RP 2Z (1998) was applied on experimental works. This recommended practice describes how to cut off CTOD specimen for analyzing after test and for quantifying the amount of coarse grain heat affected zone (CGHAZ) at the crack tip. This methodology was extended to quantify the amount of fine grain heat affected zone (FGHAZ) at the crack tip.

The fracture toughness parameter analyzed was $CTOD_m$, in welded joints with "K" bevel, at coarse grain (CGHAZ) and fine grain heat affected zone (FGHAZ). $CTOD_m$'s tests are much more meaningful regarding crack propagation than Charpy V-notch impact tests that is often made due to its lower costs. $CTOD_m$ tests were done according to ASTM E 1290 standard. $CTOD_m$ tests may be applied to tough or brittle materials, as well as steels on the tough-brittle transition temperature. $CTOD_m$ or $_m$ is the convention for CTOD on materials tested in the high toughness zone, with temperatures above of the transition temperature, according to ASTM E 1290.

This work associated stress to traditional “Step Cooling” to make a better simulation of temper embrittlement phenomenon. Because of the existent load limits of the equipment gotten to simulate the wall stress of HDT reactors in service conditions, the size of CTOD specimens were limited as well. Then, only a phenomenological assesment of the material was made, giving up any goal of getting design parameter regarding HDT reactors, according to Zumpano (2003). The thickness effect on $CTOD_m$ specimen toughness is related to the gradual transition from plane stress condition to plane strain condition. 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 took out from each one of these sections, three on the upper side and three on the lower side of the welded joint (figure 4). The final orientation of the $CTOD_m$ specimens according to BSI 7448:part 2:1997 was NQ. One third part of the bars was submitted to the “Step Cooling” associated with stress of 138,6 MPa. Another third part of the bars was submitted to the traditional “Step Cooling” and on the remnant bars no embrittlement simulation were made. Before the final $CTOD_m$ specimen machining, metallographic analysis were done at the bars to localize CGHAZ and FGHAZ with the goal of giving the correct direction to notch placement by machining and the correct direction of the fatigue pre-crack of $CTOD_m$ specimens.



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 4: Position to take the bars out from rectangular sections transversally to the welding progress direction, according to Zumpano (2003).

After testing, API RP 2Z (1998) methodology for verifying the microstructural HAZ region hit by the crack tip was taken. Seventeen $CTOD_m$ specimens were tested without "Step Cooling". Eighteen $CTOD_m$ tested specimens were treated by traditional "Step Cooling". Other fourteen $CTOD_m$ specimen were tested after "Step Cooling" with stress of 138,6 MPa associated to it. Another twelve $CTOD_m$ tests on the base metal (BM) were done. $CTOD_m$ specimens crack surfaces were analyzed at scanning electronic microscope (SEM) to verify fracture mechanisms.

4. Results and Discussion

Figure 5 compare hardness values of different welded joints regions in each treatment simulation.

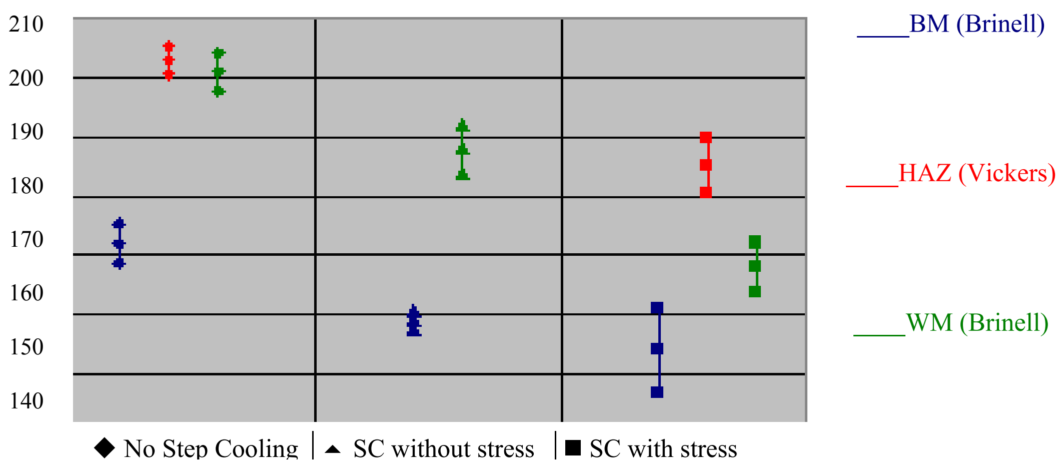
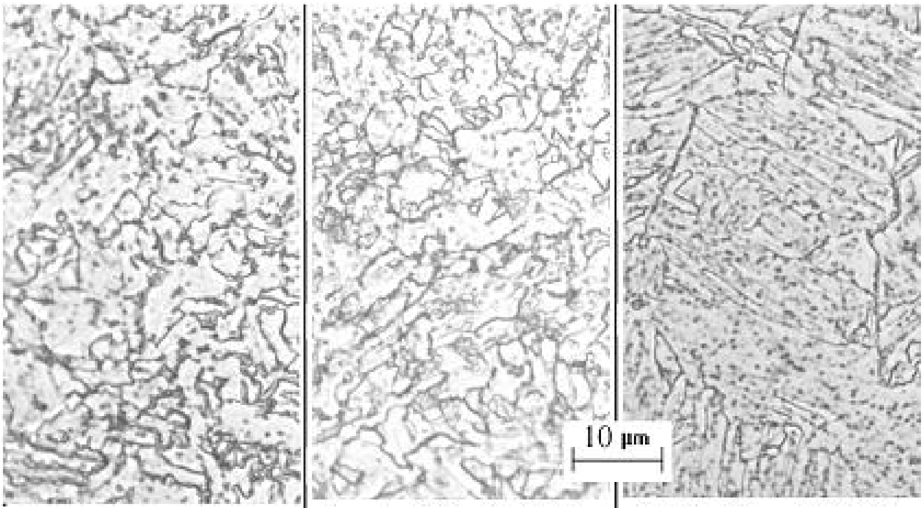


Figure 5: Hardness results of different welded joints regions (BM – base metal; HAZ – heat affected zone; WM – weld metal) in each treatment simulation: without Step Cooling (SC), SC without and with stress. According to Zumpano (2003).

The hardness values reduction of the specimens after "Step Cooling", mostly after "Step Cooling" associated with stress may be observed. At figure 6 may be seen, side-by-side, the microstructure of samples at three different treatment.



Sample 1F – CGHAZ
Step Cooling with stress

Sample 6F – CGHAZ
Step Cooling without stress

Sample 9C – CGHAZ
without Step Cooling

Figure 6: Microstructure of CGZAC at three different treatment conditions. Nital 2% - (Zumpano - 2003).

Carbide precipitation and coalescence may be seen in the grain boundaries and in the matrix at CGHAZ, at figure 6, 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 WM.

CTOD values met at base metal were about 6% lower than HAZ values met at the same condition, without "Step Cooling". The difference on $CTOD_m$ tests means that HAZ and BM values are in the same range if considering standard deviation. The welded joint was made with a small heat input according to original WPS. $CTOD_m$ tests results for HAZ at different treatment simulation showed closed values at the three situations if considering standard deviation, the values are on the same range (figure 7).

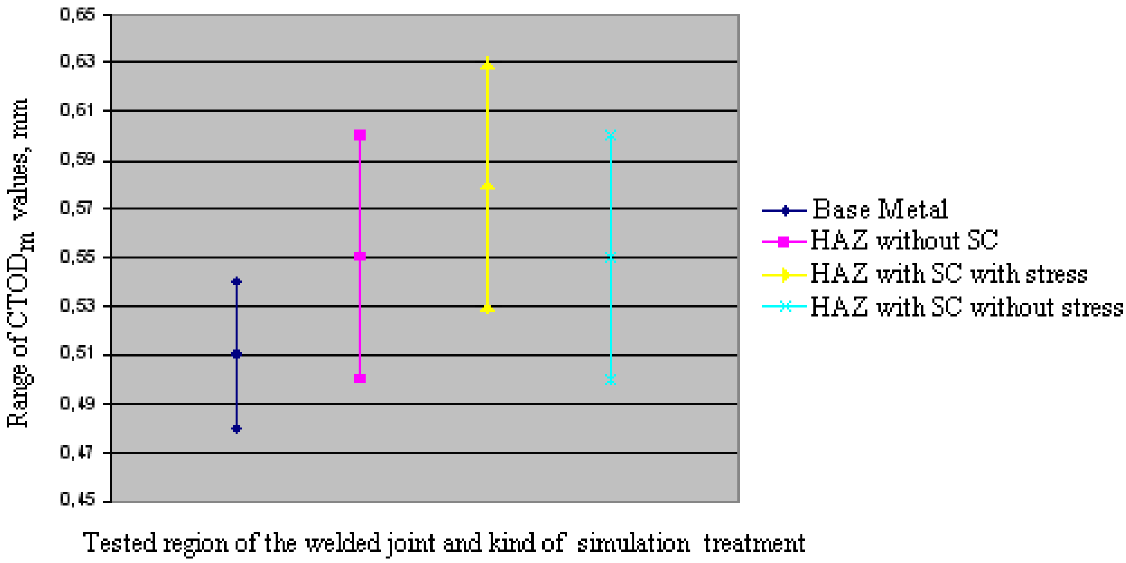


Figure 7: $CTOD_m$ values (average ± standard deviation) gotten on BM and HAZ for three different treatments according to Zumpano (2003).

No significant differences on fracture toughness values, perceptible on $CTOD_m$ tests, regarding to the different microstructures of HAZ could be observed (figure 7). $CTOD_m$ test values did not show significant differences comparing when fatigue pre-crack tip hit CGHAZ and when it hit FGHAZ for the three treatment conditions. 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, and possibly that the welding procedure generates few CGHAZ and much FGHAZ (figure 8).

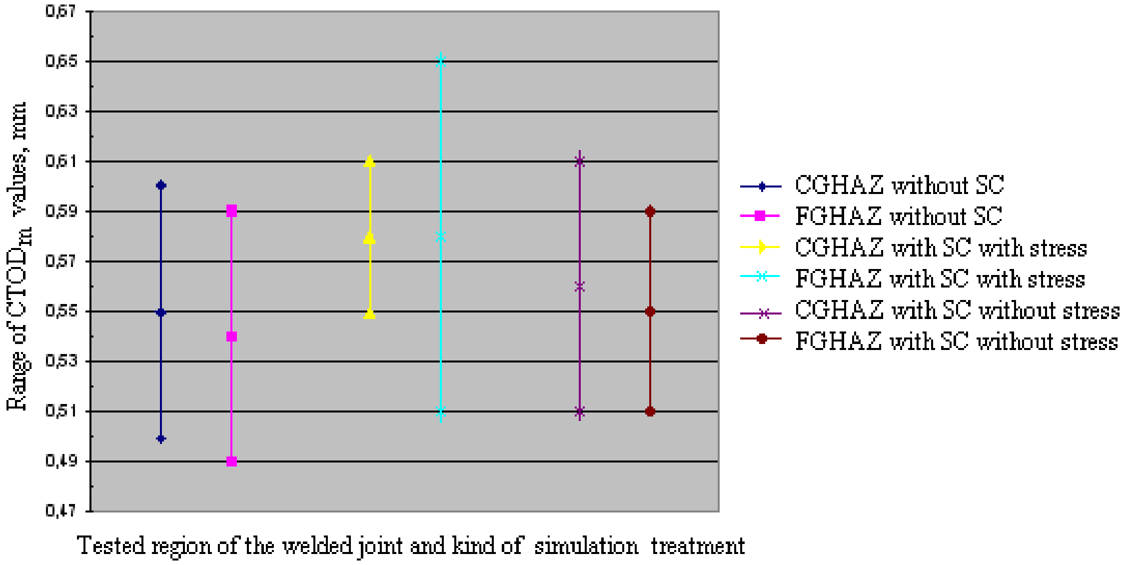


Figure 8: Comparison of $CTOD_m$ values (average ± standard deviation) at CGHAZ and at FGHAZ in three treatment conditions (SC = Step Cooling), according to Zumpano (2003).

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 figure 9.

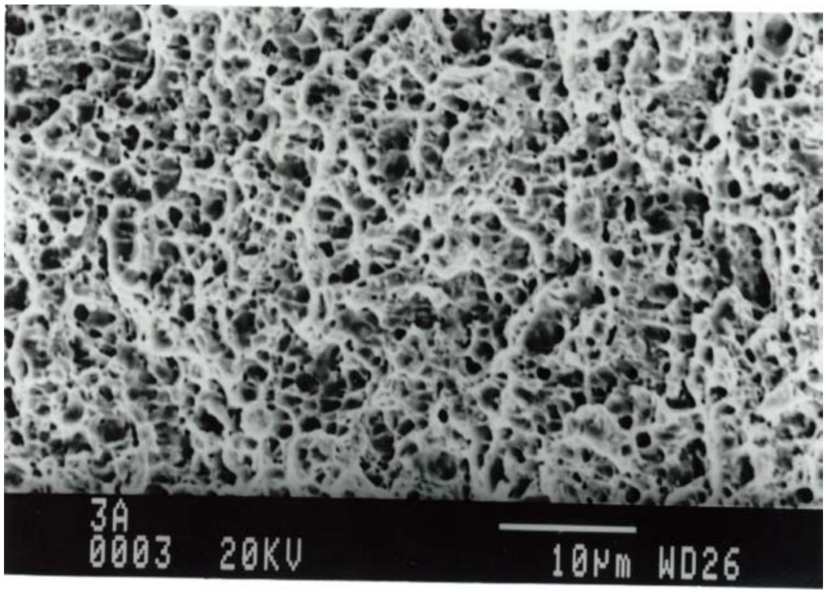


Figure 9: Fractography (SEM) of crack surface of $CTOD_m$ specimens, region of stable crack growth at sample 3A – FGHAZ – with "Step Cooling" with stress, according to Zumpano (2003).

5. Conclusions

Hardness reduction at CTOD specimens with Step Cooling may be explained for 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 the use as design parameters to HDT reactors, but they are valid for the material behavior analysis simulating in service conditions of the vessel.

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 MPT.

Microstructural differences between HAZ regions did not implicate in variations at fracture toughness values perceptible by means of $CTOD_m$ tests done.

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