

EVALUATION OF HEAT AFFECT ZONE IN SUPERMARTENSITIC STAINLESS STEEL

AVALIAÇÃO DA ZONA TERMICAMENTE AFETADA DO AÇO INOXIDÁVEL SUPERMARTENSÍTICO

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ABSTRACT

Nowadays, there is a strong trend for exploiting oil and gas in places that demand a high level of operation complexity. This includes, for example, the presence of high levels of contaminants (mainly carbon dioxide, CO₂, and sulphide, H₂S), high temperature and pressure. All these difficulties have forced companies to search for new exploration technologies. Supermartensitic stainless steels are already used as casing/tubing in production wells. Now, they appear as an alternative material for pipe line, due to their good corrosion resistance and weldability. Moreover, when compared to Super Duplex steels for this application, they are more economical due to their lower production cost. This study contributes to the understanding of the microstructure of HAZ, the most critical zone of a weld, of this steel. The Thermo-Calc® software was used as a tool to analyze the formation of the HAZ. The obtained data were qualitatively correlated to the microstructure of the material submitted to three different welding heat inputs. Three main regions with different characteristics were identified in the HAZ. At the highest temperatures, Region A is characterized by the complete transformation of the material to ferrite with a strong grain growth. In Region B, a partial transformation of austenite into ferrite occurs forming a two-phase region ($\gamma + \delta$). In the region C, complete austenitizing occurs close to the peak temperature. On cooling, this austenite transforms to martensite (not tempered).

KEYWORDS: Supermartensitic, HAZ-regions, Thermo-Calc®, microstructure, weldability

RESUMO

Atualmente, há uma forte tendência para a exploração de petróleo e gás em locais de elevado nível de complexidade de operação. Isto inclui altos níveis de contaminantes (principalmente CO₂ e H₂S), alta temperatura e pressão. Todas essas dificuldades forçam à busca por novas tecnologias. Os aços inoxidáveis Supermartensítico já são utilizados como tubing e casing e aparecem como uma alternativa para linhas de condução, devido à sua boa resistência à corrosão e soldabilidade. Além disso, quando comparado ao aço Super Duplex, eles são mais econômicos, devido ao seu menor custo de produção. Este estudo contribui para a compreensão da microestrutura da ZTA. O software Thermo-Calc foi utilizado como uma ferramenta para analisar a formação do ZTA. Os dados obtidos foram correlacionados de forma qualitativa com a microestrutura do material submetido a três diferentes ciclos térmicos de soldagem. Três principais regiões com características diferentes foram identificados na ZTA. Em temperaturas mais elevadas, a região é caracterizada por uma transformação completa do material em ferrita delta com um forte crescimento de grãos. Na Região B, uma transformação parcial da austenita em ferrita ocorre formando uma região de duas fases ($\delta + \gamma$). Na região C, austenitização completa ocorre perto da temperatura máxima. No resfriamento, essa austenita se transforma em martensita (não temperada).

PALAVRAS-CHAVE: Supermartensítico, ZTA, Thermo-Calc®, microestrutura, soldabilidade

INTRODUCTION

Nowadays, there is a strong trend for exploiting oil and gas in places that demand a high level of operation complexity. This includes, for example, the presence of high levels of contaminants (mainly carbon dioxide, CO₂, and sulphide, H₂S), high temperature and pressure. These difficulties are forcing companies to seek for new exploration technologies. Martensitic stainless steels are already used as production tubing, because they present good mechanical properties and CO₂ corrosion resistance. However, these conventional martensitic steels are susceptible to H₂S corrosion and do not have a good weldability. Therefore, they are limited to applications where welding and resistance to H₂S are mandatory.

To ensure a better performance, new generations of martensitic stainless steels have been developed, and one of them is Supermartensitic stainless steel (SMSS). This relatively new alloy ensures improved mechanical properties and corrosion resistance compared to those of conventional martensitic stainless steels. It also provides a better weldability. Another key point is the cost of these steels. Supermartensitic stainless steels are an alternative to duplex stainless steels considering its potential for cost reduction [JACKMAN, 1995, SMITH, 1999]. Due to these characteristics, it has been much required by the oil industry as an alternative for line pipe applications, where welding is extremely important.

Supermartensitic stainless steels are based on the Fe-Cr-Ni-Mo system, having low levels of C, N, P and S. They can be classified into three classes: low-Cr, Ni and Mo (11% Cr, 2.5% Ni, 0.1% Mo), medium content of Ni and Mo (12% Cr, 4.5% Ni and 1.5% Mo), and high content of Ni and Mo (12% Cr, 6.5% Ni and 2.5% Mo) [RODRIGUES, 2005]. The basic concept to improve generalized and localized corrosion resistance is to increase the effective chromium content in the matrix by reducing carbon content. Addition of nickel stabilizes the austenite and prevents the presence of delta ferrite in the microstructure. However, when in excess, nickel leads to the presence of retained austenite, because it lowers the final martensite formation temperature (M_f) below the room temperature. Although molybdenum stabilizes ferrite and decreases the M_s temperature, its addition is important to increase the resistance to general corrosion and to SSC. With the lower level of carbon content, the possibility to improve the weldability of steel is expected. Furthermore, better corrosion resistance and good toughness can be achieved in the weld joint with these changes comparing with the conventional steel, because the hardness level of the HAZ is restricted [KONDO, 2002].

This work aims to evaluate to contribute to improve the understanding of the formation of the HAZ in supermartensitic stainless steels. It analyzes the changes in the region during the welding thermo cycle, and compares the results from metallographic analysis of real welds with those obtained from phase diagrams built using a commercial thermodynamic modeling program.

1. METHODOLOGY

The alloy studied was produced at Villares Metals as 180 mm diameter bars, rolled at V & M do Brazil to Ø139.7 mm outside diameter and 10.54 mm wall thickness (139.7 x 10.54 mm). After rolling the pipes were heat treated and samples were taken out in sequence for laboratory welding tests. The chemical composition is shown in Tab. 1.

Table 1: Chemical composition (in wt%).

C	Cr	Ni	Mo	Mn	Si
0.012	12.09	5.89	1.93	0.49	0.26

To contribute to improve the understanding of the heat affected zone formation in supermartensitic stainless steels, simulations were performed in the Thermo-Calc® software (version 4) using the database TCFE5. These allowed build phase diagrams presenting the tendency of different phases transformation at different temperatures. Information obtained through this program was correlated qualitatively with samples submitted to different welding thermal cycles and prepared for metallographic analysis using optical microscopy and scanning electron microscopy.

Initially, bead-on-plate welds trials were made to determine welding parameters with TIG (GTAW) process with heat input levels: 0.5, 1,5 and 2.8 kJ/mm. Results from the metallographic examination of the welds obtained in these trials, along with the diagrams built using the Thermo Calc software, were used to evaluate the microstructures present in the HAZ of this steel resulting from different welding conditions. General aspects of the microstructure were analyzed, including the precipitates characterization, through optical microscopy and scanning electron microscopy.

2. RESULTS

2.1. Thermo-Calc evaluation

Fig. 1 uses a diagram that presents the variation of the content of different phases with temperature as a tool to characterize the regions that occur in the HAZ of a supermartensitic stainless steel. This figure is based on a methodology presented in the Welding Handbook of the American Welding Society. This methodology relates the temperature peak reached by each point of the heat affected zone with the temperature of equilibrium diagram. It is assumed that, for each point, its constitution at high temperature will be given, in a first estimate, by the corresponding region of the diagram. Using this methodology, it can be supposed that there the HAZ zone of a supermartensitic stainless steel is formed by three or four regions.

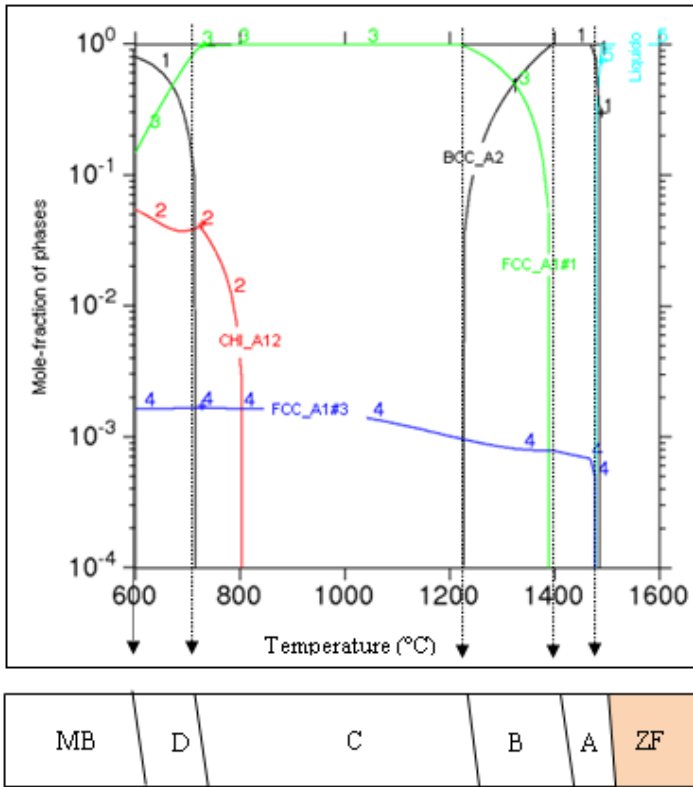


Figure 1: Schematic figure of HAZ formation.

2.2. Thermal Cycles Simulation

Fig. 2 shows the thermal cycles obtained by simulation for the different welding conditions used in the work. As expected, slower cooling conditions are predicted for welding with higher heat input. To estimate the time at high temperature, the peak temperature was set arbitrarily, in the modeling, to 1400°C. Tab. 4 shows the values of 800 and 500°C ($\Delta t_{8/5}$) and above 1220°C estimated by the simulation.

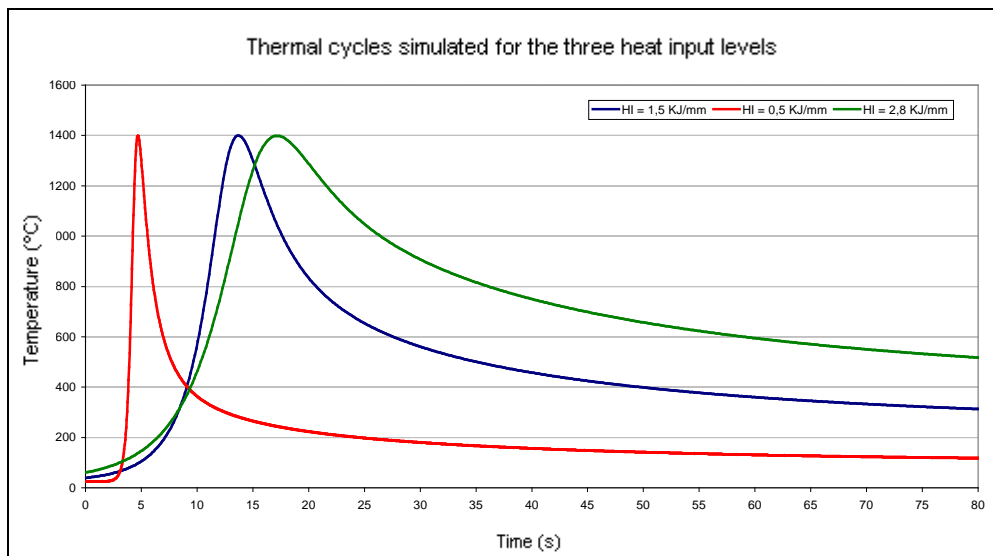


Figure 2: Thermal cycles simulated for the three heat input levels.

The simulation indicates that the time above 1220°C for the condition with the highest heat input was about five times longer than that for the test with the lowest heat input, and approximately twice that of the weld with $H_i = 1.5$ kJ/mm. These results show, as expected, the possibility of a larger grain growth during welding with the highest heat input. Furthermore, the $\Delta t_{8/5}$ is approximately 30 times longer for during welding with 2.8 kJ/mm than that expected when welding with $H_i = 0.5$ kJ/mm and three and a half times longer when compared to the welding with $H_i = 1.5$ kJ/mm. This indicates a greater probability of intermetallic precipitation that may affect the properties and corrosion resistance of the joint during welding with the highest heat input [LADANOVA, 2006].

Thus, increasing the heat input increases also the time at high temperature and decreases the cooling rate. A long time at higher temperature should allow, in Region A, a higher grain growth of ferrite and thus reduce the tendency of material transformation during cooling because there is a reduction in grain boundary area available to start the austenite formation. In Region B, a longer time at high temperature may allow a greater diffusion of ferrite stabilizing elements to this phase, increasing its stability and reducing its tendency to transform cooling. On the other hand, a slower cooling rate would allow more time for the ferrite transformation into austenite to occur during cooling. Therefore, the amount of ferrite in these regions that remains after cooling should depend on the relative influence of the time at high temperature and the cooling rate for each region.

2.3. Microstructural Evaluation

The HAZ microstructures obtained with the three different energy levels are shown in Fig. 3. In supermartensitic stainless steels, the HAZ tends to present a high complexity even in single pass welding. In general, the structure of the joint consists in a fusion zone and HAZ divided in regions A, B and C as previously proposed. The HAZ regions formed at high temperatures are discussed in greater detail below.

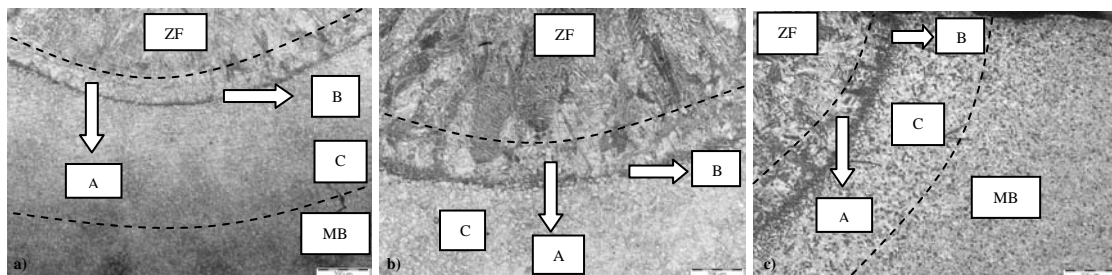


Figure 3: Microstructure at different heat inputs: a) 0.5 kJ/mm; b) 1.5 kJ/mm and c) 2.8 kJ/mm.

- Region A

In the region A, which is associated to the highest peak temperatures in the HAZ (Fig. 1), the complete transformation of the material to ferrite should occur, i.e., this region will be formed by 100% ferrite under the heat source. During exposition to this high temperature, a strong grain growth is expected to occur. A region with the presence of both liquid and solid at high temperature is expected to form near the fusion line. However, it should be very thin since the solidification range of this steel solidification is relatively narrow. The microstructure evolution of region A during welding should follow the following sequence: During the heating of the base metal, the austenite begins to transform in δ ferrite at temperatures above approximately 1224°C and this transformation should be completed above 1390°C. When the single phase region is formed, ferrite grains starts to growth. At high temperatures (around 1400°C), the equilibrium should be approached quickly and it is reasonable to assume that the ferrite has a homogeneous composition.

During cooling, some quantity or all δ ferrite, should transform into austenite which transforms to martensite with cooling down M_s . Depending on the cooling conditions and the austenite formation kinetics, it should preferably be formed from the ferrite grain boundary. The austenite resulted from the δ ferrite decomposition may occur in different morphologies [CARROUGE, 2002]. It may occur basically with the allotriomorphic morphology, intragranular and Widmanstätten austenite. The allotriomorphic austenite is the first constituent to form in high temperatures yet, during the cooling, in the ferrite grain boundaries. It's possible to obtain also the intragranular austenite. The formation of intragranular austenite occurs if the pre-existing ferrite has a much greater grain size than the austenite being formed and there are sites for intragranular nucleation. In this condition, austenite grains can be formed into the ferrite. Another constituent present is the Widmanstätten austenite. It is formed at lower temperatures than the other and is composed of parallel plates that nucleate at delta ferrite grain boundaries or allotriomorphic austenite pre-existing and grow along well-defined plans of the matrix. Fig. 4 shows the microstructure of region A.

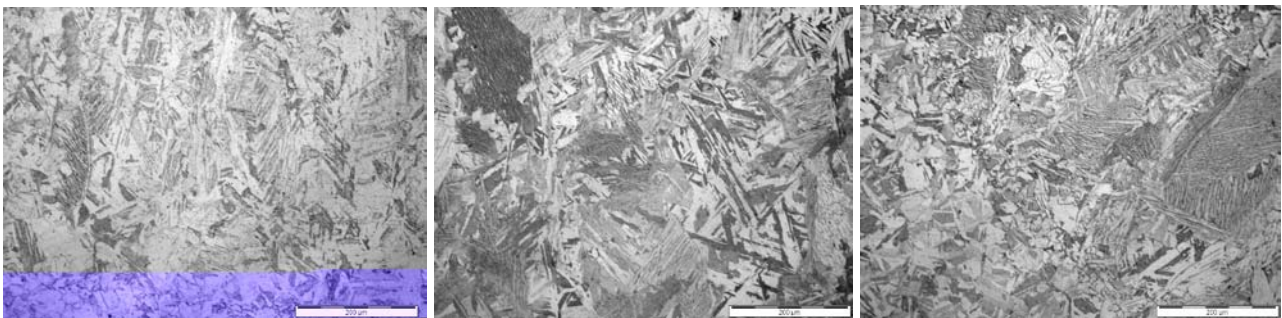


Figure 4: Region A microstructure: a) HI = 0.5 kJ/mm; b) HI = 1.5 kJ/mm and c) HI = 2.8 kJ/mm.

The austenite formed will be transformed at the end of cooling to martensite, and may remain as a fraction of retained austenite. The martensite formed is not tempered and present higher hardness than the base metal. It may also happen the carbides precipitation, particularly at grain boundaries and in the remaining ferrite regions. No significant difference was observed in relation to the microstructure for different levels of energy applied in the material.

- Region B

Region B is submitted to peak temperatures between about 1224 and 1390°C. In this range, there is a partial transformation of austenite into ferrite, forming the two-phase region ($\delta+\gamma$). Part of ferrite formed can remain in HAZ depending on the cooling rate and transformation kinetics. Having been only partially ferritized, the Region B must present a smaller grain size than the region A. Between the temperature range indicated, the growth grain should be limited because the material remains in two phases region. The delta ferrite should start former from the grain boundaries of previously existing austenite, which leads to intergranular morphology for that. The mechanism of ferrite formation is diffusionless according to the literature [CARROUGE, 2002], and it tends to be enriched in elements such as chromium and molybdenum. Thus, in the region partly ferritized, the amount of δ ferrite remaining untransformed after cooling will be influenced by the amount of chromium and molybdenum present and also by cooling rate. According with Carrouge, 2002, higher cooling rates favor a greater amount of ferrite retention, whereas lower rates allow greater dissolution of this.

Thus, this region may be formed predominantly by non-tempered martensite, possibly with areas with different morphologies, may still be parts of ferrite and eventually retained austenite. Fig. 5 shows micrographs of region B with presence of δ ferrite for different heat inputs with applied. The

etching Lichtenegger-Bloch (LB) [MARTIN, 2007] was used to show this constituent. Fig. 5 shows micrographs of region B obtained for the different heat input levels used in the present work

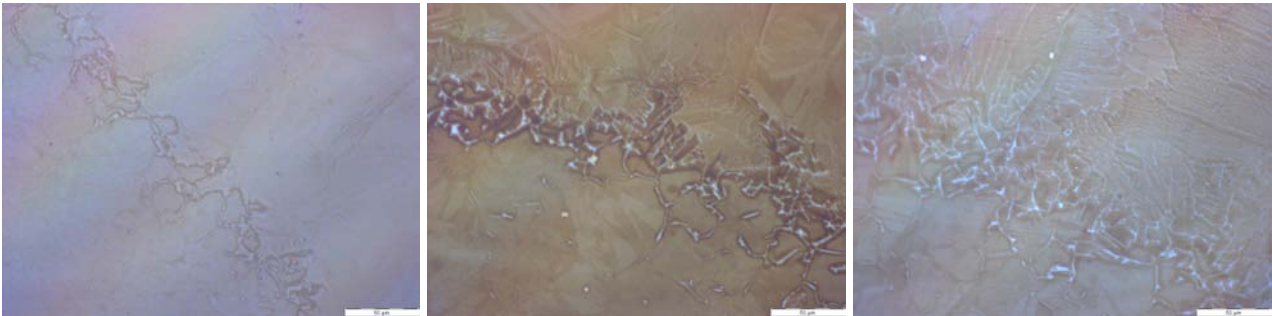


Figure 5: Region B microstructure: a) HI = 0.5 kJ/mm; b) HI = 1.5 kJ/mm and c) HI = 2.8 kJ/mm.

- Region C

Region C transforms completely to austenite during the heating. During cooling, this austenite transforms back to martensite (not tempered). Again, depending on the welding thermal cycle and the characteristics of the phase transformations, some untransformed austenite may remain in this region. Fig. 6 shows the microstructure of region C.

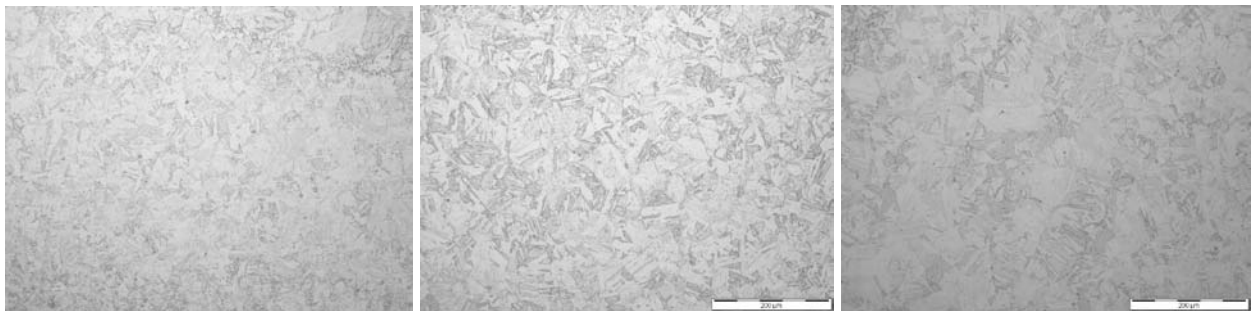


Figure 6: Region C microstructure. a) HI = 0.5 kJ/mm; b) HI = 1.5 kJ/mm and c) HI = 2.8 kJ/mm.

- Region D

The region D was predicted by Thermo-Calc® as a region where there was possibly of a higher tempering, but it was not confirmed through metallographic analysis. It means, that were not found in this study, clear evidence of a super temper region or a partial austenitization. Fig. 7 shows the microstructure of region D.



Figure 7: Region D microstructure: a) HI = 0.5 kJ/mm; b) HI = 1.5 kJ/mm and c) HI = 2.8 kJ/mm.

It is important to remember that for regions in the HAZ formed at lower temperatures (region C and D, for example), a separate analysis on the Thermo-Calc® may not be sufficient for these inferences because the material can not get close to equilibrium conditions. However, it should still work with a guideline. Therefore, it is expected that the response give by Thermo-Calc® is more appropriate to evaluate the characteristics of regions A and B of the ZTA, as they are formed at high temperatures, which favors achieve conditions close to equilibrium.

- Base Metal

The metal base, as shown in Fig. 8, presents a homogeneous microstructure formed by tempered martensite with precipitates of Ti (C, N). These precipitates are formed at high temperatures, mostly before and during the solidification. They have a relatively coarse size, a polyhedral format and a reddish color, typical of this carbonitride. The EDS analyzes are shown in Fig. 9, which confirm that these precipitates have a composition expected for titanium carbonitride.

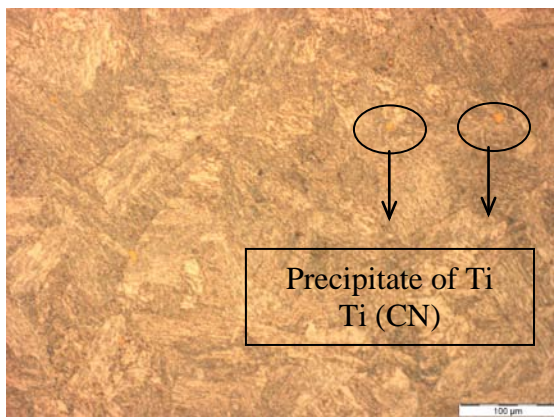


Figure 8: Metal base microstructure: Base metal

3. CONCLUSIONS

In this work, the study of supermartensitic stainless steel with the Thermo-Calc® program has provided important information about the expected phases in different temperature ranges, which was used to make inferences about the formation of the HAZ during welding. Three regions with different characteristics were identified using the software.

In region A, there is the complete transformation in ferrite during the welding thermal cycle. This transformation occurs above 1390°C and is accompanied by a strong grain growth. The austenite resulted from the delta ferrite decomposition occurs in different morphologies, such as allotriomorphic, intragranular and Widmanstätten austenite.

Region B shows, between 1224°C and 1390°C, the partial transformation of austenite into ferrite, thus forming a two-phase region ($\gamma + \delta$). With a small grain size, the region B was partially ferritized during heating with limited grain growth.

In Region C occurs the full austenitizing during heating between 716°C and 1224°C. On cooling, the austenite transforms to martensite again (not tempered).

The region D shows the microstructure quite similar to the base metal. It was predicted by Thermo-Calc® as a region where there was possibly of a higher tempering, but it was not confirmed through metallographic analysis.

4. REFERENCES

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