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Influence of Heat Treatments on the Impact Toughness of a Ti-stabilized 12%Cr Supermartensitic Stainless Steel

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The supermartensitic stainless steels (SMSS) are a relatively new class of corrosion resistant alloys developed to obtain a better combination of weldability, strength, toughness and corrosion resistance than conventional martensitic stainless steels. The final properties of SMSS are strongly influenced by quenching and tempering heat treatments. In this work, different routes of heat treatments were tested in a Ti-stabilized 12%Cr supermartensitic stainless steel with the objective to improve mechanical properties, specially the low temperature (-46°C) toughness. Double and triple quenching were tested and compared to single quenching heat treatments. Two tempering temperatures (500°C and 650°C) were tested. The results obtained with instrumented Charpy impact tests showed that a triple quenching treatment was able to increase the density of fine TiC particles and improve the mechanical properties of specimens heat treated by quenching and tempering at 650°C.

Keywords: *Supermartensitic stainless steels; heat treatment; instrumented Charpy; embrittlement*

1. Introduction

The supermartensitic stainless steels (SMSS's) have an interesting combination of weldability, strength, toughness and corrosion resistance. For certain service conditions it's considered as an economical alternative for duplex and superduplex stainless steel in the oil and gas exploration industry[1]. These steels have excellent properties due to the lowered carbon content (< 0.03%) and increased Ni content (up to 6%).

Some new SMSS grades also contain Mo addition to increase mechanical strength and corrosion resistance. Nb and/or Ti can also be added as stabilizing element to form carbides and nitrides. According to Rodrigues et al.[2] TiC fine carbides promote the refinement of the microstructure and increase the mechanical properties. Boron addition refined the microstructure and increased the hardness and wear resistance by M_2B precipitation[3].

The mechanical properties of martensitic steels are adjusted by quenching and tempering heat treatments. Toughness is one of the properties which is most affected by these treatments. In previous works[4-5] it was observed the temper embrittlement phenomena in SMSS 13%Cr tempered in the 400°C - 600°C range. This type of embrittlement is easily observed in conventional martensitic stainless steels tested at room temperature[6], but in SMSS the temper embrittlement was only perceptible in impact tests at lower temperatures, such as -46°C[4-5]. A simple, but possible, explanation for this is the higher purity of SMSS compared to conventional martensitic stainless steels.

Toughness is a key property for new applications of SMSS. In this work, new routes of quenching are proposed to improve the toughness of a Ti-alloyed SMSS. In parallel to instrumented impact tests, careful microstructural analysis was performed to discuss and explain the results.

2. Experimental

The material studied was from a seamless tube of SMSS with 200 mm of diameter and 10 mm thickness The chemical composition was determined by combustion method (C, S and N) and plasma spectroscopy (other elements), as shown in Table 1.

Pieces of the tube were cut in specimens of 57 x 11 x 8.5 mm for heat treatment. Three routes of quenching were performed, as explained in Table 2. Q1 is a single quenching (1000°C), Q2 is a double quenching (1000°C and 900°C) and Q3 is a triple quenching treatment (1000°C, 900°C and 800°C). According to a previous dillatometric analysis the Ac_3 temperature of the steel is 727°C[5], which suggest that the lower soaking temperature chosen for quenching (800°C) was above Ac_3.

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Table 1: Chemical composition of the supermartensitic stainless steel studied (%wt).

C	Cr	Ni	Mo	Mn	Ti	P	S	N
0.028	12.21	5.8	1.95	0.52	0.28	0.011	0.001	0.01

Table 2: Quenching treatments.

Specimen	Quenching treatments
Q1	1000ºC-1h/water quenching (WQ)
Q2	1000ºC-1h/WQ + 900ºC-40 min./WQ
Q3	1000ºC-1h/WQ + 900ºC-40 min./WQ + 800ºC-40 min/WQ

After quenching Q1, Q2 or Q3 the specimens were tempered. Table 3 shows specimen identification accordingly to the tempering treatment.

Table 3: Tempering treatments and specimens identification.

Quenching	Tempering		
	500ºC/1h	600ºC/1h	650ºC/1h
Q1	Q1-500	Q1-600	Q1-650
Q2	Q2-500	Q2-600	Q2-650
Q3	Q3-500	Q3-600	Q3-650

After the heat treatments the specimens were machined to the final dimensions of subsize Charpy impact tests (55 x 10 x 7.5 mm) with V notch[6].

Detailed investigation by scanning electron microscopy (SEM) was conducted in samples polished and etched with Villela's reagent (90 ml H_2O, 10 ml HCl, 1 g picric acid ($C_3H_3N_3O_7$). The austenite volume fraction of specimens Q1-650, Q2-650 and Q3-650 were determined by magnetization saturation tests following the procedure suggested by Cullity[7] and used in previous works[4,5]. Electron backscattered scanning diffraction (EBSD) was performed in specimens Q1, Q2 and Q3 to determine the previous austenite grain sizes, but only a qualitative result was obtained, as will be shown.

Thermodynamic calculations with Thermocalc® using TCF6 database were performed to preview thermodynamic stable phases at selected temperatures between 500ºC and 1000ºC. A simplified chemical composition of the steel was used in this analysis: 0.028%C, 12.21%Cr, 5.8%Ni, 1.95%Mo, 0.28%Ti (%wt).

Vickers hardness tests were performed with load 30 kgf.

The Charpy instrumented tests were performed in an Instron SI-ID3 machine with maximum capacity of 400 J and precision of ± 0.5 J. The pendulum speed was 5.184 m/s. The specimens were cooled to -46°C and maintained for five minutes before the tests. Three specimens per condition were tested, and average values are presented in the results. The main results of instrumented Charpy tests are the initiation, propagation and total energies, and the load *versus* time or deflection curve.

3. Results and discussion

Figure 1 shows the load *versus* deflection curve of specimen Q3, where it is possible to distinguish 3 stages. The areas of these portions correspond to three distinct energies:

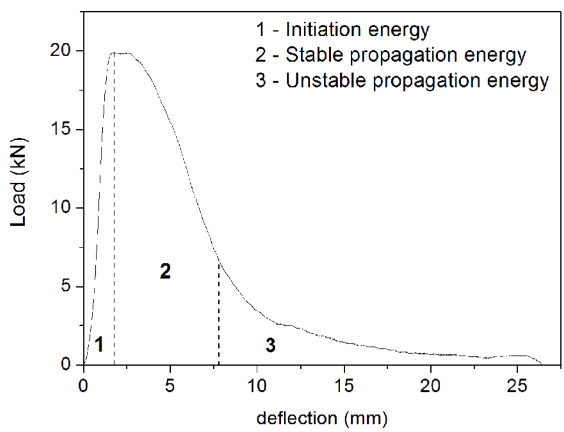

Figure 1: Load x deflection curve of specimen Q3.

- Energy 1 - Initiation Energy;
- Energy 2 - Stable propagation energy of the crack;
- Energy 3 - Unstable propagation energy of the crack.

The initiation energy corresponds to the area of the curve from the origin to the maximum load, and represents the energy used in the process of crack initiation. The propagation energy can be divided into stable (2) and unstable (3), and the boundary between then corresponds to the inflection point of the curve. Conceptually, the instability of the crack starts at the "failure point". The determination of this exact point is not always an easy task. The sum of the three portions is the total energy required to fracture in the Charpy test.

Figure 2 shows a comparison between the initiation, propagation (stable and unstable) and total energy of specimens Q1, Q2 and Q3. The propagation energy and the total energy increases from Q1 to Q3. In these three specimens the propagation energy represents the major portion of the total energy, and also increases from Q1 to Q3. The increase of toughness with the double and triple quenching treatments can be subject of discussion. As a first hypothesis, a grain refinement effect may be inferred. For instance, Xiong et al.[8] obtained a significant reduction of austenitic grain size and martensite lath width with double quenching treatment of low carbon high Cr and W steel. The comparison between Figures 3(a) and (b) suggests that Q3 (Figure 3(b)) has a finer microstructure than Q1 (Figure 3(a)). However, a quantitative EBSD analysis of these fields was not conclusive about the austenite grain size refinement with the double and triple quenching, because some of the boundaries revealed in Figures 3(a) and (b) are from the previous austenite and other boundaries are from the martensite packets.

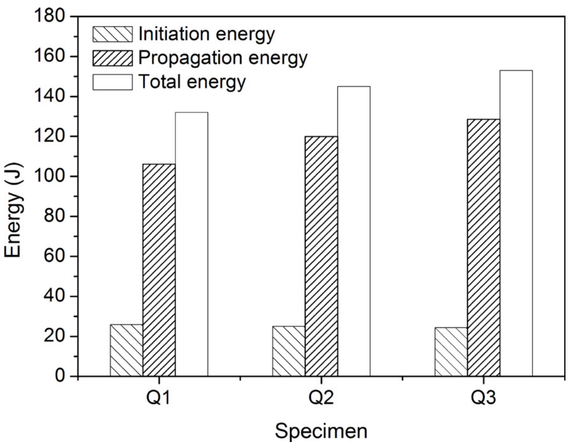

Figure 2: Initiation, propagation and total energies of specimens Q1, Q2 and Q3.

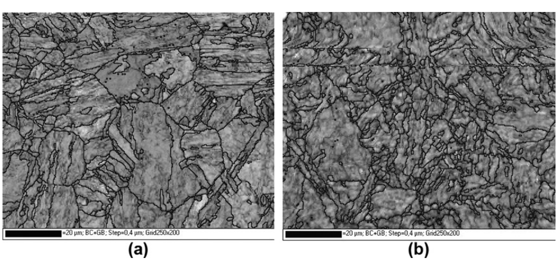

Figure 3: SEM image of (a) Q1 and (b) Q3.

The Thermocalc® analysis based on the chemical composition of the steel determined the phases more stable thermodynamically as function of temperature, as shown in Table 4. Comparing the final quenching temperatures of specimens Q1 (1000°C), Q2 (900°C) and Q3 (800°C) it is previewed the increase of the amount of TiC from 1000°C to 800°C and formation of chi phase at 800°C. Figures 4(a-b) confirm the increase of the amount of TiC particles from Q1 to Q3, which can also be a reason to the increase of toughness in the same order. Mo-rich chi phase was not observed in specimen Q3 in the SEM analysis.

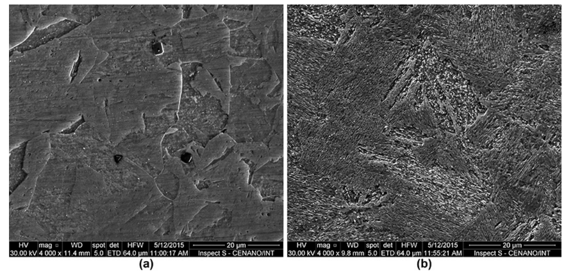

Figure 4: Specimens (a) Q1 and (b) Q3. (Square particles in Q1 are TiN precipitates).

Table 5 shows the Vickers hardness and the total impact energy results of all specimens investigated. The additional TiC precipitation in specimens double and triple quenched was not sufficiently fine to provoke hardening. On the contrary, the increase of the density of these particles in the microstructure reduces the carbon content in solid solution and provokes the decrease of hardness from Q1 to Q3.

Table 5: Vickers hardness results.

Specimen	Vickers hardness (HV30)
Q1	311 ± 3
Q2	298 ± 5
Q3	278 ± 4
Q1-500	326 ± 2
Q2-500	305 ± 2
Q3-500	300 ± 4
Q1-650	279 ± 2
Q2-650	262 ± 2
Q3-650	262 ± 2

Figure 5 shows a comparison between the load *versus* deflection curves of specimens Q3, Q3-500 and Q3-650. In Figure 6, the initiation, propagation and total energies for these three specimens were compared. The low toughness of Q3-500 is attributed to a temper embrittlement effect. Figure 7 shows a comparison of impact energies of specimens tempered at 500°C and 650°C. All specimens tempered at 500°C had low impact energies, but the triple quenched

Table 4: Thermocalc® analysis for the steel composition in five temperatures of interest (% wt of phases).

Phases	800°C	900°C	1000°C	650°C	500°C
Ferrite	0	0	0	61.93	90.91
Austenite	99.35	99.85	99.86	33.51	0
TiC	0.16	0.15	0.14	0.16	0.15
Chi phase	0.49	0	0	4.40	8.25
Ni_3Ti	0	0	0	0	0.69

(Q3-500) has a higher impact toughness, which suggests that the higher amount TiC carbides precipitated in the triple quenching caused a reduction in the embrittlement effect.

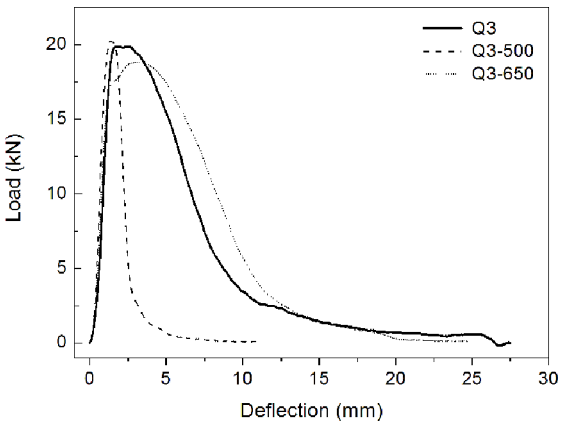

Figure 5: Comparison between the curves of load x deflection obtained in the instrumented Charpy tests of specimens with triple quenching Q3, Q3-500 and Q3-650.

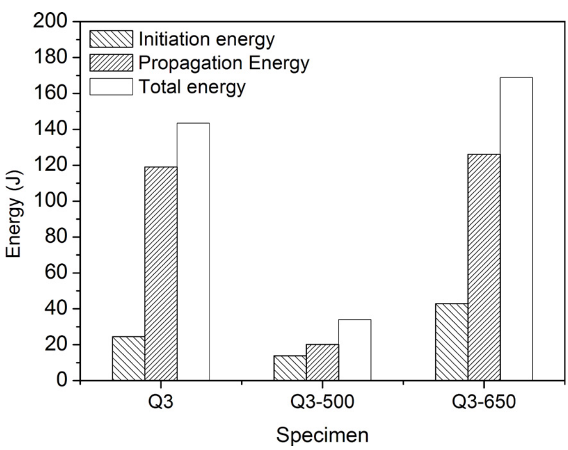

Figure 6: Initiation, propagation and total energies of specimens triple quenched (Q3, Q3-500 and Q3-650).

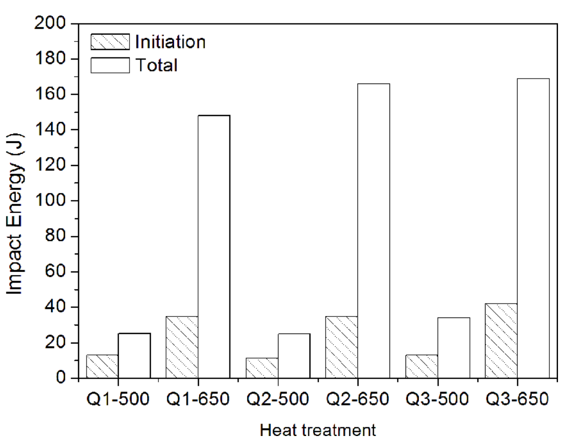

Figure 7: Initiation and total energies of specimens quenched at 500ºC and 650ºC.

The triple quenching also promoted an increase of the impact toughness of the specimen tempered at 650ºC (Q3-650). Curiously, according to the data of Table 6, the amount of austenite of specimen Q3-650 is considerably lower than those of Q1-650 and Q2-650, which can be explained by the higher amount of TiC particles produced by the triple quenching treatment. These results indicate that the austenite content is not the only and, probably, not the more important factor to increase the toughness of SMSS's.

Table 6: Magnetization saturation (m_s) and austenite volume fraction (C_γ) determined by magnetic method in specimens Q1-650, Q2-650 and Q3-650.

Property	Q1-650	Q2-650	Q3-650
m_s (emu/g)	162.6	160.1	170.5
C_γ	0.076	0.090	0.031

The minimum toughness of specimens tempered at 500ºC is also coincident with an increase of hardness, i.e., the steel also presents a small secondary hardening effect, which is related to fine additional precipitation during the tempering treatment. According to the Thermocalc® study, 4.4% of chi phase should precipitate at 500ºC, and 8.25% at 650ºC. In duplex and superduplex stainless containing Mo chi phase produces deleterious effects on toughness and corrosion resistance[9]. However, the high toughness of specimen Q3-650 is a strong evidence of the absence of chi phase in the microstructure. The formation of chi at 500ºC would be more difficult than at 650ºC from the point of view of kinetics. On the other hand, very fine precipitates, not restricted to grain boundaries, can be observed in a specimen quenched and tempered at 500ºC, as shown in Figure 8. These precipitates were not identified, but they are likely responsible for the secondary hardening. Further investigation is needed to identify these particles, including as possibilities the additional fine TiC precipitation and Ni_3Ti, as suggested by the Thermocalc® analysis (Table 4).

Figure 9(a) shows the macrograph of the surface fracture of specimen Q3-500 after the Charpy test. The fracture occurred with 0.6 mm of lateral expansion and 41.7% of brittle area. When the tempering embrittlement is caused by impurities segregation in grain boundaries or is due to an intergranular precipitation, is commonly observed intergranular cracks in the surface of cracking. This is not to the present case, since the SEM analysis of the brittle area revealed a quasi-cleavage feature, without intergranular cracks (Figure 9(b)). This fact reinforces the hypothesis that the temper embrittlement is caused by the same fine precipitates which caused secondary hardening (Figure 8).

4. Conclusions

Supermartensitic steel with 12%Cr was submitted to different heat treatments. A triple quenching treatment with

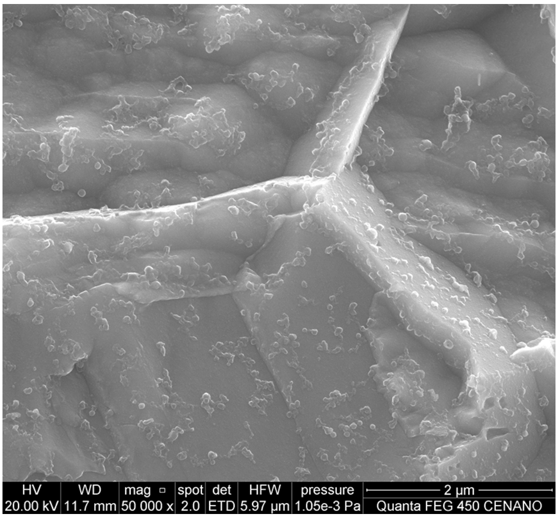

Figure 8: SEM image of specimen Q3-500 with small precipitates.

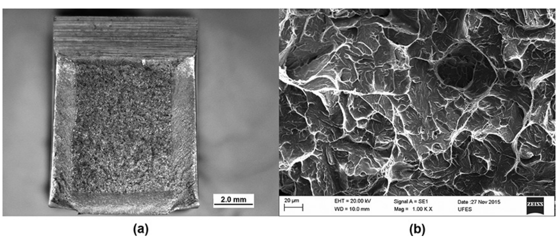

Figure 9: Analysis of the fracture surface of specimen Q3-500: (a) macrograph; (b) SEM analysis of the brittle portion.

austenitizing temperatures 1000ºC, 900ºC and 800ºC increased the amount of TiC carbides in the martensitic matrix. In a comparison with specimens double quenched (1000ºC and 900ºC) and single quenched (1000ºC), the specimen triple quenched (1000ºC, 900ºC and 800ºC) has higher toughness and lower hardness. Nevertheless, the tempering at 500ºC causes embrittlement due to fine precipitates which also provokes secondary hardening. Triple quenching treatment reduced the effect of temper embrittlement at 500ºC and further increased the impact toughness of the specimen quenched at 650ºC. The specimen triple quenched and not tempered also has interesting properties due the microstructure of soft martensite and high density of TiC carbides.

5. Acknowledgements

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