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Influence of heat treatments on the sensitization of a supermartensitic stainless steel

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Abstract

Supermartensitic stainless steels with 12-13% Cr show higher corrosion resistance than conventional grades such as UNS S42000 and S41000. The reduction of carbon content to less than 0.03%, and the addition of Ni and Mo are the most important compositional changes which enhances mechanical properties and corrosion resistance. Ti addition is used to combine with C and N, and avoid Cr carbides precipitation and to improve mechanical properties. In general, SMSS steels are quenched and tempered or double tempered. The purpose of this work was to investigate how the microstructure and the corrosion decay by sensitization are influenced by quenching and tempering heat treatments in a novel supermartensitic 13% Cr stainless steel with Ti addition. DL-EPR (double loop potentiokinetic electrochemical reactivation) test was used to obtain the degree of sensitization (DOS). The results show that, despite the extra low carbon content, and the stabilization with Ti, the material can become sensitized with heat treatments. The sensitization is rather related to Ti(C, N) precipitation and reverse austenite than to Cr carbides.

Keywords: Supermartensitic steels; microstructure; intergranular corrosion; sensitization.

1. Introduction

Supermartensitic stainless steels (SMSS) with 12-13% Cr show higher corrosion resistance than conventional grades such as UNS S42000 and S41000. The reduction of carbon content to less than 0.03%, and the addition of Ni and Mo are the most important compositional changes which enhances mechanical properties and corrosion resistance [1].

Sensitization can be defined as intergranular chromium carbide precipitation which causes Cr depletion in the vicinity of grain boundaries. As a consequence, the steel becomes susceptible to intergranular corrosion when exposed to aggressive environments. These Cr-depleted regions present a weakest passive layer, with an anodic behaviour in front of the unaffected zones [2-5]. In fact, sensitization may not be restricted to chromium carbides precipitation but also includes other Cr rich phases [6-8]. Besides, although intergranular precipitation is more common, intragranular precipitates may also cause chromium depletion and localized corrosion.

Supermartensitic steels must be quenched and tempered, or double tempered, to achieve optimum mechanical properties. The heat treatments also change the corrosion resistance of the steel. Different types of corrosion, such as pitting, intergranular and stress corrosion cracking are connected and closely related to microstructural features. In particular, precipitation reactions may provoke sensitization and corrosion decay. Although SMSSs are less susceptible than conventional stainless steels, some works have shown that these extra low carbon materials can also become sensitized [5,9-12]. Nakamichi *et al.* [5] studied the intergranular corrosion cracking in the heat affected zone (HAZ) of a 11% Cr SMSS, and found

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that the extension of the Cr depleted zone was about 10 to 15 nm. Ladanova *et al.* [9] also measured the width of the Cr-depleted zone and found about 25 nm around $M_{23}C_6$ carbides in the as welded HAZ. After post weld heat treatment (PWHT) at 640ºC the Cr depletion was eliminated due to the diffusion (healing). Aquino *et al.* [10] and Della Rovere *et al.* [11] studied the sensitization of weld joints of SMSS using double loop electrochemical potentiodynamic reactivation tests (DL-EPR). In a previous work of our group this technique was also used to analyse a Ti-alloyed SMSS [12].

The addition of Ti and/or Nb is supposed to increase the intergranular corrosion resistance of SMSS, as already observed in austenitic [13] and ferritic stainless steels [14,15]. However, even stabilized steels may undergo sensitization, as observed in previous works [11,12,16].

The purpose of this work was to investigate how the microstructure and the degree of sensitization of a novel SMSS 12% Cr stainless steel with Ti addition are influenced by quenching and tempering. In a previous work, the effect of tempering treatments after quenching from 1000ºC was investigated [12]. In this work, double and triple quenching treatments were tested in order to produce new and finer microstructures. After quenching treatments, single and double tempering treatments were performed.

2. Materials and Methods

The material used in the study was obtained from a seamless tube of Ti alloyed 13% Cr SMSS with chemical composition shown in Table 1.

Table 1. Chemical composition of 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

The temperatures M_s (martensite start), M_f (martensite final), A_1 and A_3 were determined by dilatometry using cylindrical specimens with 6.00 mm diameter and 10.00 mm length. The heating rate applied was 5ºC/min.

The specimens were cut and machined with 15x15x 10 mm dimensions for double loop electrochemical potentiodynamic (DL-EPR) tests. Before the confection of working electrodes for DL-EPR, the specimens were heat treated.

Three quenching treatments were performed, as shown in Fig. 1. Q1 is a single water quenching with soaking at 1000ºC for 1 h. Q2 is a double quenching treatment, with the same cycle of Q1, followed by a second soaking at 900ºC for 1h and water quenching. Q3 is a triple quenching treatment, with the same cycles of Q2, followed by a third quenching with soaking at 800ºC. After quenching, some specimens were single or double tempered according to Table 2.

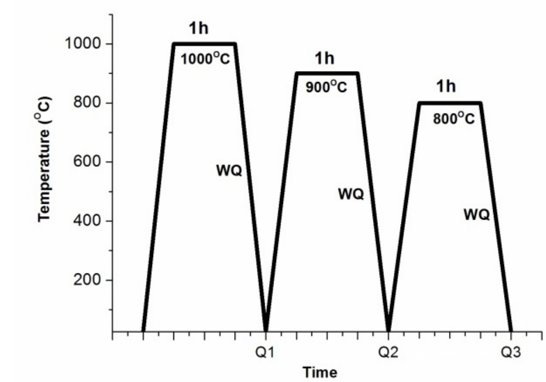

Fig. 1. The quenching treatments performed.

The DL-EPR tests were carried out in a conventional three cell electrode assembled with working electrode, Pt foil as auxiliary electrode, and saturated calomel electrode (SCE) as reference. The working electrode was constructed using the supermartensitic specimens embedded in epoxy resin with a cooper wire for electric contact. Usually, the working electrodes were ground with 400 emery paper and cleaned in water. However, some electrodes were polished with diamond paste in order to observe the surface after test in the scanning electron microscope (SEM). The tests were controlled by a potentiostat-galvanostat. The test solution was composed of 0.25 mol/L H_2SO_4 + 0.01 mol/L KSCN. Before the test, the open circuit potential (E_{OCP}) was stabilized for 30 min. The potential was then increased in the anodic direction at 1 mV/s up 0.3 V_{SCE}. Then, the scan was reversed, using the same sweeping rate in the cathodic direction. The parameters extracted from the DL-EPR were the Ir/Ia and Ar/Aa ratios, where Ir and Ia are the peak currents in the reactivation and activation peaks, and Ar and Aa are the areas of the reactivation and activation loops, respectively. According to the literature, these two parameters give a measure of the degree of sensitization (DOS) of the steel [17]. In this work the Ir/Ia and Ar/Aa were compared. The tests were done in triplicate, using three specimens per heat treatment condition. Average values are presented in the results.

Microstructural investigation was performed by optical and scanning electron microscopy (SEM). The microstructures were revealed by Villela's etching (95 mL ethanol, 5 mL HCl and 1 g picric acid). Some