Continuous cooling sensitization and its evaluation in austenitic stainless steel EN 1.4310

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Abstract

Sensitization in stainless steels is caused by chromium depleted zones near grain boundaries which can lead to intergranular corrosion and intergranular stress corrosion cracking in service. A lot of work has been done in the past to understand sensitization behavior under isothermal conditions. However, this study aims at studying the sensitization behavior in continuous cooling, which is of more practical importance in steel production and in heat treatments such as welding. Conditions for sensitization were determined using experiments (Double-Loop Electrochemical Potentiokinetic Reactivation tests (DL-EPR)) and then compared with DICTRA simulations. Using these conditions a continuous cooling sensitization (CCS) diagram is determined for EN 1.4310 (301) austenitic stainless steel. DICTRA is a CALPHAD based simulation software used for diffusion related studies in multicomponent alloys. Solvus temperature for $M_{23}C_6$ is determined to be 959 °C.

Keywords: sensitization, continuous cooling, austenitic stainless steel, DICTRA

1. Introduction

Austenitic stainless steels find wide applications in industry due to their good weldability, superior corrosion resistance and creep resistance. But the steels, when subjected to temperatures in the range 450 – 900 ^oC, are prone to intergranular corrosion and intergranular stress corrosion cracking as a result of sensitization. This is primarily due to the development of chromium depleted zones as a result of the formation of $M_{23}C_6$ precipitates on the grain boundaries[1][2]. The severity of intergranular corrosion depends on depth of Cr depletion profile at the interface between austenite matrix and the formed carbides [2]. A lot of work has been done in the past to understand sensitization behaviour under isothermal conditions. However, this study aims at studying sensitization resulting from continuous cooling, which is of more practical importance in steel production and in heat treatments such as welding. Continuous cooling sensitization (CCS) predictions that are based on isothermal test data are not accurate and cannot estimate the degree of sensitization (DOS) properly [4]. Also, isothermal data cannot estimate the effect of peak temperature on CCS. Therefore, in this work continuous cooling experiments have been performed. The development of Cr depleted zones during continuous cooling was characterized using double-loop electrochemical potentiokinetic reactivation tests (DL-EPR). This is possible because the results of the DL-EPR test depend on width and length of the Cr depleted zone [3]. The results are rationalized using DICTRA simulations.

2. Materials and experimental procedures

The material used in this study was EN 1.4310 austenitic stainless steel with the chemical composition in wt.%: 0.105 C, 16.8 Cr, 6.36 Ni, 0.95 Si, 1.20 Mn, 0.3 Cu, 0.065 N. The alloy was solution treated at 1100 °C for two hours. Specimens of length 180mm, width 50mm and thickness 2mm were made from the homogenized alloy. The thermal cycles shown in Table 1 were performed on these samples using a Gleeble 3800® thermo-mechanical simulator. The specimens were heated to the peak temperatures with a heating rate of 50 °C/s, held for 2 seconds and then cooled to room temperature with cooling rates of 0.125, 2 and 32 °C/s.

Heating rate (°C/s)	Peak temperature (°C)	Holding time at peak temperature, s	Cooling rates (°C/s)
50	700, 800, 900, 1000	2	0.125, 2, 32

Table 1. The thermal cycles employed

Following thermal cycling the specimens were subjected to DL-EPR tests [6][7][8] at room temperature using 0.5M H_2SO_4 + 0.01M KSCN as the test solution and a scan rate of 1.67 mV/sec. The degree of sensitization is the ratio of the peak current density during the reactivation scan to the peak current density during activation scan. When DOS < 0.01 , the alloy is considered to be unsensitized, when DOS lies in between 0.01 and 0.05, the alloy is slightly sensitized and might pass the Strauss tests. When DOS is more than 0.05, the alloy is highly sensitized and would probably fail Strauss tests [5].

Numerical simulations were performed using the CALPHAD (CALculation of PHAse Diagrams) based DICTRA® software package, which is used for the simulation of diffusion controlled transformation in multicomponent systems. The simulations assume local equilibrium at the moving phase interface and solve multicomponent diffusion equations using thermodynamic and kinetic databases [9]. The numerical simulation was reduced to one-dimensional problem by assuming that $M_{23}C_6$ grows with a planar morphology along the grain boundary at the interface between austenite matrix and the carbide. The thermodynamic calculations required for the simulations were performed in a Thermo-Calc® software package. Following references [10] and [11], the initial width of the austenite matrix was set to one sixth of the grain size, which in the present alloy is 48μm. $M_{23}C_6$ was added to the left of the austenite matrix as an inactive phase at the start of simulation. The TCFE7 module was used for thermodynamic data and MOBFE2 was used for kinetic data. The TCFE7 database together with Thermo-Calc was used to determine the solvus temperature for $M_{23}C_6$ in the steel composition studied. The solvus temperature for $M_{23}C_6$ is calculated as 959 °C.

3. Results and discussion

3.1 Degree of sensitization

Figure 1 shows the variation of (DOS) with peak temperatures for different cooling rates. The trend is the same for all the cooling rates and is highest for samples heated to and cooled from 900°C. As DOS is directly related to the susceptibility to intergranular corrosion, this implies that the samples continuously heated to and cooled from 900 °C are most prone to intergranular corrosion. The samples that are cooled from 1000 and 700 °C with a cooling rate of 32 °C/sec are unsensitized and those cooled from 900 and 800 °C with a cooling rate of 32 °C/sec are slightly sensitized. All the other samples with DOS greater than 0.05 are highly sensitized. So the cooling rate should be higher than 32 °C/sec to avoid sensitization when the samples are cooled from a peak temperature of 900 °C.

Peak temperatures (°C)/ Cooling rates (°C/sec)	0.125	2	32
1000	0.197	0.047	0.013
900	0.204	0.147	0.029
800	0.167	0.109	0.026
700	0.079	0.030	0.009

Table 2. DOS values measured from DL-EPR tests

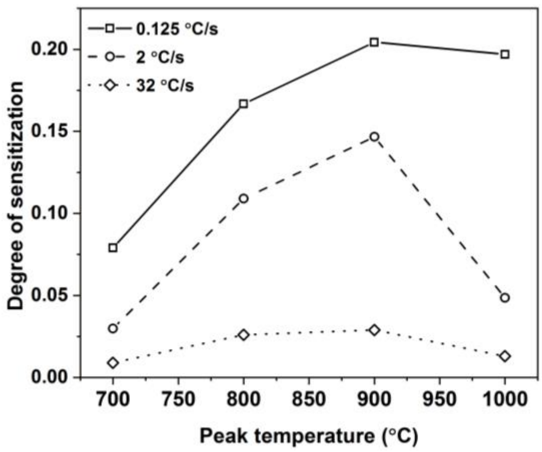

Figure 1. Variation of DOS with peak temperatures for different cooling rates

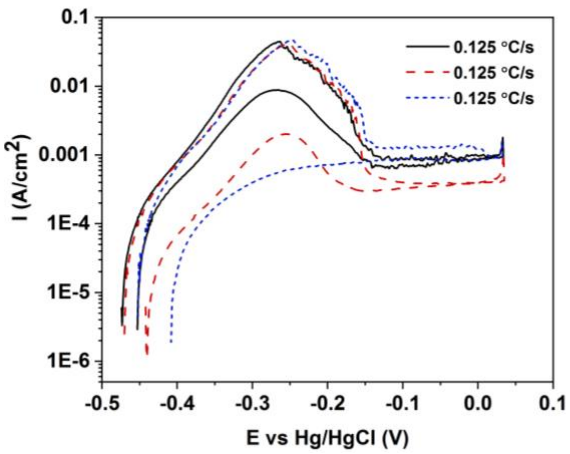

Figure 2. DL-EPR curves for different cooling rates and at peak temperature of 1000 °C

3.2 Effect of heating rate

Bearing in mind the fact that the solvus temperature for $M_{23}C_6$ is calculated as 959°C, the reason for highest DOS when the peak temperature is 900 °C can be attributed to the formation of carbides during the heating cycle as suggested by Solomon et al., [4][12]. Carbide nucleation at such high heating rates as 50 °C/s can probably be attributed to the high C content in the alloy. When coming to peak temperatures of 1000 °C, some of the carbides formed on heating will re-dissolve resulting in lower DOS values, reducing the effect of the heating stage. Therefore, DICTRA simulations were performed for the peak temperature of 1000°C assuming that there is no effect of the heating stage, i.e. by considering homogeneous material starting at 1000°C and cooled from that peak temperature. Figure 2 shows DL-EPR curves for the samples that were cooled from 1000 °C. The curve corresponding to the high cooling rate of 32 °C/s does not show any reactivation peak, i.e. there is no intergranular corrosion and the sample is unsensitized.

3.3 Continuous Cooling Sensitization diagram

DICTRA simulations were performed following the procedure described above for cooling from the peak temperature 1000 °C. The Cr concentration profiles across the interface from the carbide into the austenite matrix are shown in Figure 3. Following the procedure described Sourmail et al [10] and Tokunaga et al [11] the average weight percentage of Cr in the austenite in the 25 nm thick layer adjacent to the interface (a_{25nm}) has been calculated rather than the mean over the first 20 nm suggested by Stawström and Hillert[11]. Table 2 shows the values obtained together with the experimentally determined DOS values. Comparing these values, it can be seen that when a_{25nm} is greater than 13.5, then the alloy is unsensitized, when $11.5 < a_{25nm} < 13.5$, then the alloy is

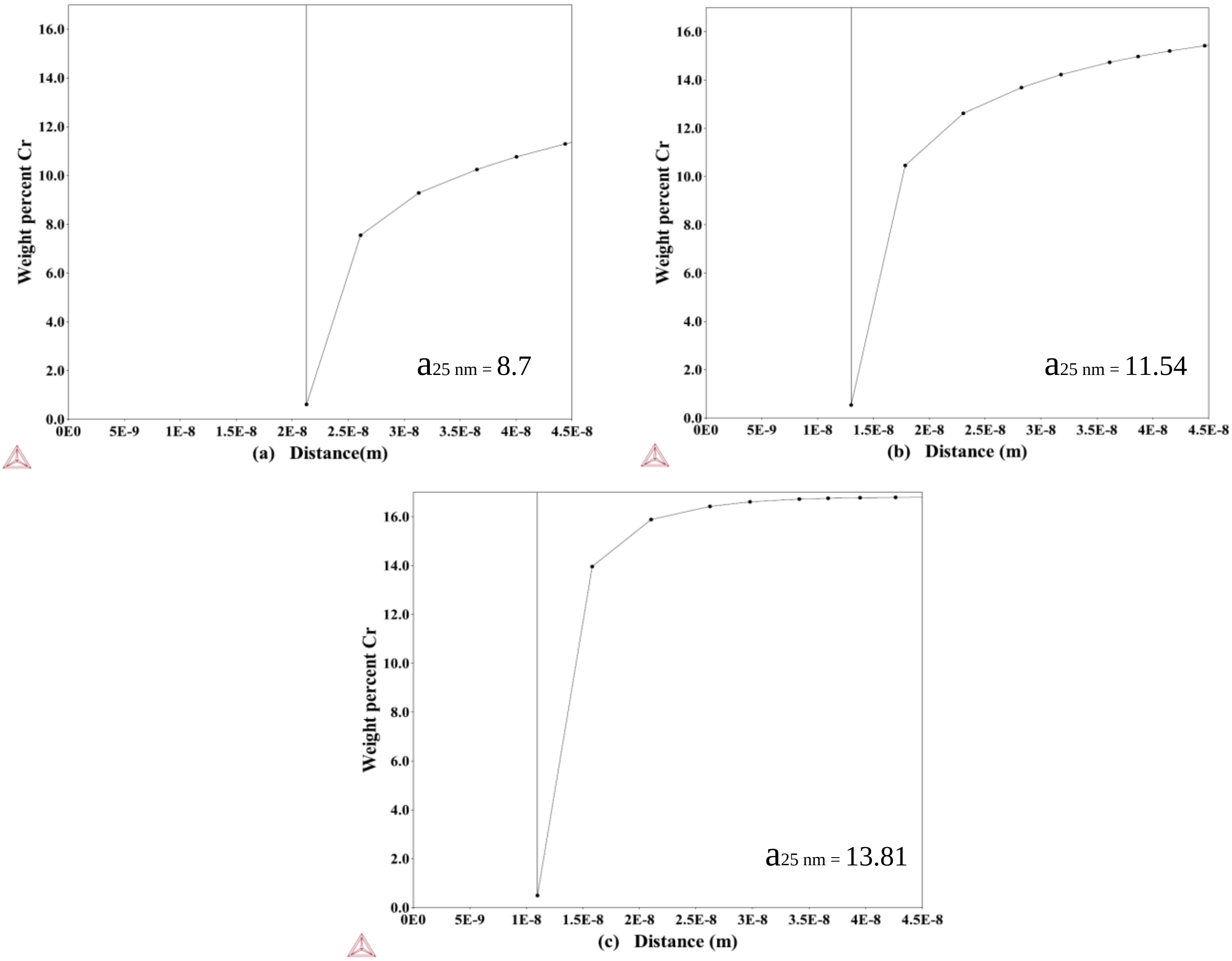

Figure 3. DICTRA simulations showing Cr concentration profiles across the interface between $M_{23}C_6$ and austenite after continuous cooling from 1000 °C to 400 °C with a cooling rate of (a) 0.125 °C/s (b) 2 °C/s (c) 32 °C/s

slightly sensitized and when a_{25nm} is less than 11.5, then the alloy is highly sensitized. Based on these conditions, simulations were performed for different cooling rates to different temperatures allowing a continuous cooling sensitization diagram to be plotted for the peak temperature of 1000 °C, see Figure 4. The simulations were only performed down to 400 °C since diffusion is negligible below this temperature and no further change in susceptibility will occur. As expected, it can be observed that a cooling rate of 32 °C/s should avoid sensitization when the alloy is continuously cooled to room temperature. Cooling at around 2 – 8 °C/s to room temperature should cause slight sensitization. All cooling rates below 0.5 °C/s are predicted to cause high sensitization when cooling to room temperatures. Besides predicting the intergranular corrosion behavior of the alloy EN 1.4310 when it is cooled to room temperature, Figure 4 can also be used to predict DOS if cooling is stopped at higher temperatures. The aim of future work is to experimentally test whether these predictions hold by quenching specimens from various temperatures after cooling at various rates.

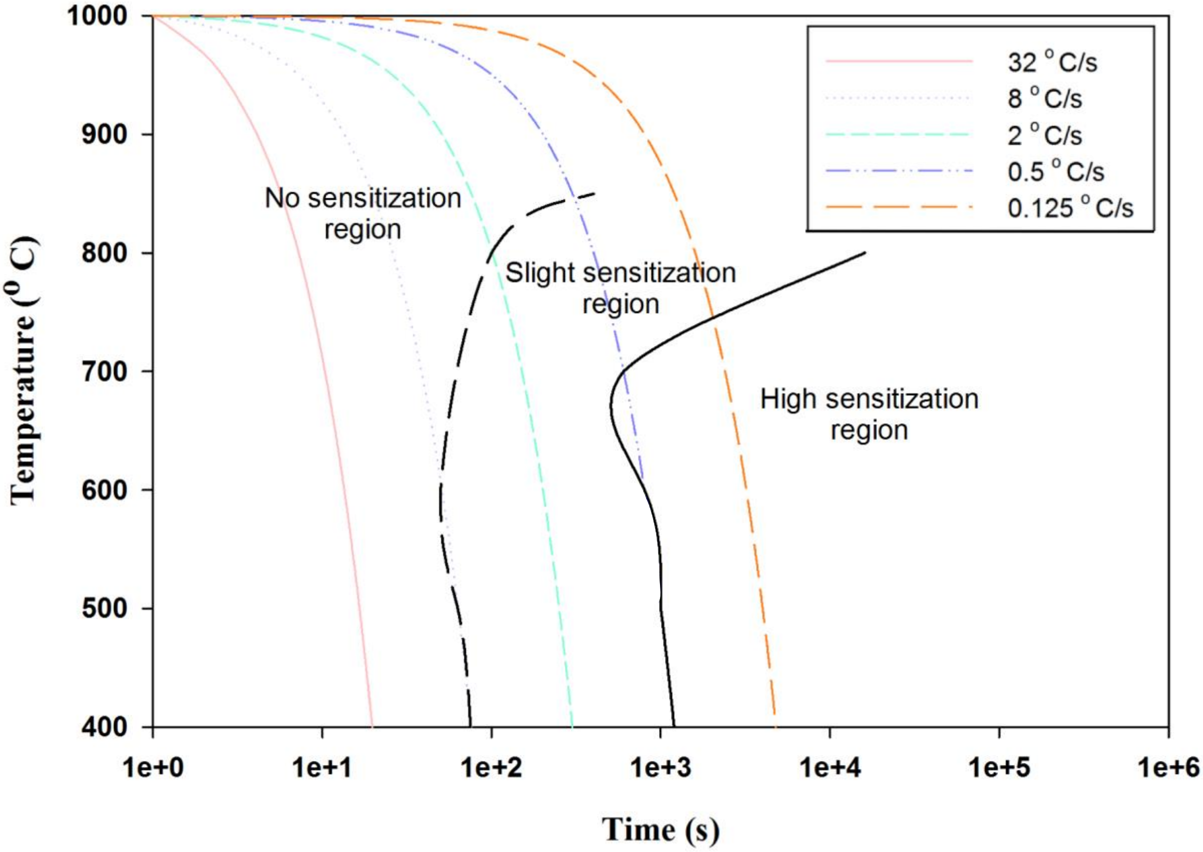

Figure 4. Continuous cooling sensitization diagram

4. Conclusions

On the basis of experimental DL-EPR measurements and Thermo-Calc DICTRA calculations of the average weight percentage of Cr in the austenite 0 - 25 nm from the carbide/austenite (a_{25nm}) suggest that the austenitic stainless steel EN 1.4310 will not be sensitized on cooling from 1000 °C provided $a_{25nm} > 13.5$ wt:%. The condition $11.5 < a_{25nm} < 13.5$ wt.% will produce slight sensitization while $a_{25nm} < 11.5$ wt.% will produce a highly sensitized microstructure. The calculated continuous cooling sensitization (CCS) diagram can be used to predict critical cooling rates across different temperature regimes.

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