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Study of Intergranular Corrosion in Austenitic Stainless Steels Using Electrochemical Impedance Spectroscopy

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***Abstract*—**Electrochemical impedance spectroscopy (EIS) has been used to detect sensitization in austenitic stainless steels that are heat treated in the temperature regime 600-820 °C to produce different degrees of sensitization in the material. The tests were conducted at five different DC potentials in the transpassive region. The quantitative determination of degree of sensitization has been done using double loop electrochemical potentiokinetic reactivation tests (DL-EPR). The correlation between EIS Nyquist diagrams and DL-EPR degree of sensitization values has been studied. The EIS technique can be used as a qualitative tool in determining the intergranular corrosion in austenitic stainless steels that are heat treated at a given temperature.

***Keywords*—**Electrochemical impedance spectroscopy, intergranular corrosion, sensitization, stainless steel.

I. INTRODUCTION:

AUSTENITIC stainless steels are the most common type of stainless steel. They are formable, weldable, and can be used from cryogenic to very high furnace temperatures. However, the corrosion resistance of these steels can be reduced by sensitization, in which chromium depleted zones are formed at the grain boundaries due to the precipitation of chromium carbides. The material is susceptible to corrosion when chromium level in these depleted zones goes below 12 wt.% [1]. Electrochemical methods can be used to quantify the degree of sensitization (DOS). These include potentiodynamic anodic polarization, potentiostatic etching technique and electrochemical potentiokinetic reactivation (EPR). Based on the scanning mode, there are two types of EPR tests: single and double loop EPR (SL-EPR/DL-EPR). In SL-EPR tests, the material is initially passivated in 0.5M H2SO4 + 0.01M KSCN at ambient temperatures for 15 min. A scan is run from the passivation potential to the corrosion potential of the sample at a scan rate of 6V/h. The passive film over the chromium-depleted area is dissolved when the chromium content goes below 12-13 wt.% thus generating larger corrosion currents [2], [3]. In DL-EPR the sample is anodically polarized through the active region into the passive region causing the formation of a passive layer. The second scan involves the reverse scanning by decreasing the potential to corrosion potential. This causes the dissolution of the passive film over the chromium depleted regions and results in the reactivation corrosion current. The ratio of the reaction current density (I_r) to the activation current density (I_a) gives the DOS [4].

EIS has been used to investigate the corrosion behavior in this work. EIS is a powerful method to characterize the corrosion resistance in stainless steels and is a non-destructive test method used to study the corrosion behavior of anodized films, coatings and inhibitors. It has also been used to study corrosion in stainless steels with different degrees of sensitization [5]-[7]. The obtained impedance spectra can be fitted to an approximate equivalent electric circuit. The charge-transfer resistance (R_{ct}) that is obtained from the Nyquist plots can provide insight into the degree of corrosion (intergranular corrosion) in the material: a low R_{ct} implies high corrosion in the microstructure. In this article, an attempt to quantify the AC impedance behavior of austenitic stainless steel with varying DOS has been made. Austenitic stainless steels with different DOS have been investigated with DL-EPR tests and EIS measurements.

II. EXPERIMENTS AND METHODOLOGY

The investigated material was a 3 mm thick commercial austenitic stainless steel of the type EN1.4310 obtained from Outokumpu Stainless Oy, Tornio, Finland. The chemical composition of the steel in wt.% was Fe-16.80Cr-6.36Ni-0.10C. The material was first solution treated at 1100 °C for 2 hours followed by water quenching. It is thus safe to assume that the material is homogenized after the solution treatment and is free of any kind of precipitates in the matrix [8]. These samples are heat treated at different temperatures to produce varying DOS in the material as shown in Table I.

TABLE I
HEAT TREATMENT TEMPERATURES AND TIMES

Temperature (°C)	Heat treatment time (h)
600	10, 24
650	6
700	10,48,120
760	6
820	10,120

The anodic polarization tests have been conducted using VersaSTAT 3 potentiostat. An initial delay has been

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maintained before starting the anodic polarization to achieve dynamic stabilization at the specimen - electrolyte interface. The samples are scanned from open circuit potential (OCP) to 1.6 V with a scan rate of 6 V/h. DL-EPR test were conducted on all the heat treated samples according to the standard EN ISO 12732 [4]. The standard mentions the ranges of DOS values defining highly sensitized, slightly sensitized and unsensitized specimens. In the DL-EPR test, the value of DOS is not sensitive to surface finish; hence the samples were polished to 600 grit finish. The anodic scan (anodic polarization) causes the dissolution of all the surface irregularities and forms a passive film over the exposed surface. The reverse scan instigates the dissolution of the passive layer at the regions that are depleted of chromium. This makes the Cr-depleted regions susceptible to corrosion and is seen in the reactivation current peak, which depends on the magnitude of Cr depletion [9], [10].

EIS measurements are made with potentiostat PalmSens3 operated by software PSTrace 5. An insulation layer has been used to expose the same surface area to the solution in all of the samples. Blue color dielectric has been used for the insulation by applying it on the sample surface and drying at 40°C for 2 h followed by the drying at room temperature for 2 days. EIS measurements were performed in solution containing 2 M H_2SO_4 and 1 M HCl. The potential amplitude was 10 mV and the testing frequency ranged from 0.01 Hz to 50000 Hz. However, due to strong noise at low frequencies (especially at potentials 0.8 V and 0.9 V), the measurements were often stopped at frequencies around 0.1 Hz.

III. Results and Discussion

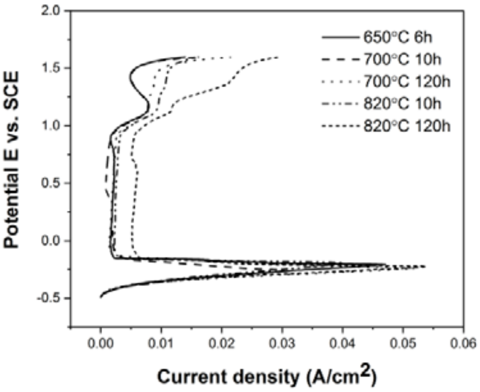

Fig. 1 Anodic polarization curves

The anodic polarization curves for all the heat treated samples can be seen from Fig. 1. All the samples heat treated at different temperatures undergo similar active - passive behavior. The passive current densities vary a bit between the samples. This is related to the quality of the passive layer that has formed during the anodic polarization. The more defective the passive layer, the higher the passive current density [11]. The transpassive regions are in the potential ranges of 800 - 1400 mV. The potentials in this range were selected and EIS tests are performed.

The DOS values obtained from the DL-EPR test can be found in Table II. This shows that the sample 700 °C/120 h was highly sensitized. In the case of heat treatment at 820°C, the decrease in DOS when heat treated to 120 h from 10 h indicates the self-healing behavior of the material. Table II shows a wide range of DOS values.

The Nyquist plots obtained from the EIS measurements can be seen in Fig. 3. The formation of capacitive and inductive loops can be observed. The size of the capacitive loop can be related to the charge-transfer resistance (R_{ct}) at the interface between the electrode and the solution. Therefore, for the first stage of investigation, all impedance spectra were fitted using simplified Randles equivalent circuit containing solution resistance (R_s), charge transfer resistance (R_{ct}) and constant phase element (CPE) as shown in Fig. 2.

TABLE II
DOS Values Obtained from the DL-EPR Testing and R_{CT} Values Obtained from the Nyquist Plots

Condition	DOS %	R_{ct} (ohms)				
		800 mV	900 mV	1000 mV	1100 mV	1200 mV
650 °C/6 h	15.1	2634	1270	857	263	26
700 °C/10 h	30.5	10380	7630	5463	335	25
700 °C/120 h	78.8	11280	12410	4721	228	30
820 °C/10 h	51.2	9908	10070	7027	250	30
820 °C/120 h	0.68	5872	12850	11540	347	41

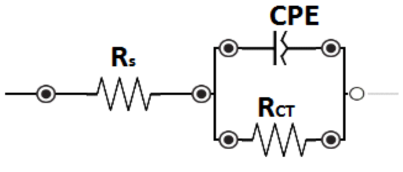

Fig. 2 Randles equivalent circuit

For the further investigations, simplified circuit will be extended to appropriate model in order to fit whole spectra. Fitted R_{ct} values are shown in the Table II. It can be observed that these R_{ct} values decrease with an increase in the DC potential at which the measurement was made. This is consistent with the increment in the current density owing to the increment in the applied potential in the transpassive region.

EIS measurements at different potentials indicate three types of AC impedance responses as is also reported by Behbahani [12]. At 800 - 1000 mV (first type), that is near the breakdown potential, the Nyquist diagram includes a single capacitive loop (Figs. 4 (a)-(c)). This region is only related to the anodic dissolution of the passive layer. The R_{ct} values are around 1200 - 13000 ohms. This indicates a high resistance and a very low dissolution rate of the passive layer. These high R_{ct} values in this region do not represent the intergranular dissolution [6]. Therefore this dissolution rate is not related to the DOS of the specimen. EIS measurement at 1100 mV (second region), includes the formation and completion of an inductive loop along with the capacitive loop (Fig. 4 (d)). That way, the EIS measurements at 1100 mV should provide useful information about the IGC behavior of the samples [12]-[15]. The Nyquist plot at 1200 mV (third type) leads to the formation of a secondary capacitive loop at low frequencies, which is related to the occurrence of pitting corrosion.

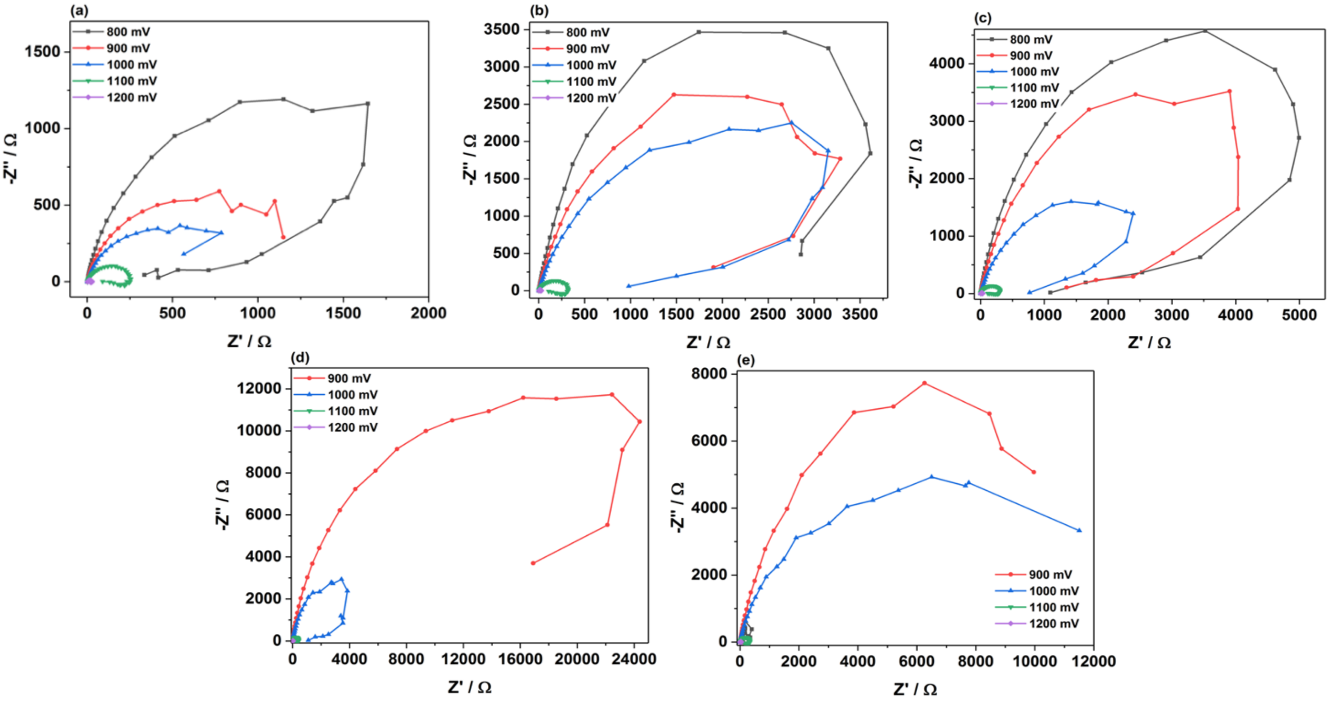

Fig. 3 Nyquist diagram of the EIS test at different potentials in the passive-transpassive transition region (a) 650°C 6 h (b) 700°C 10 h (c) 700°C 120 h (d) 820°C 10 h (e) 820°C 120 h

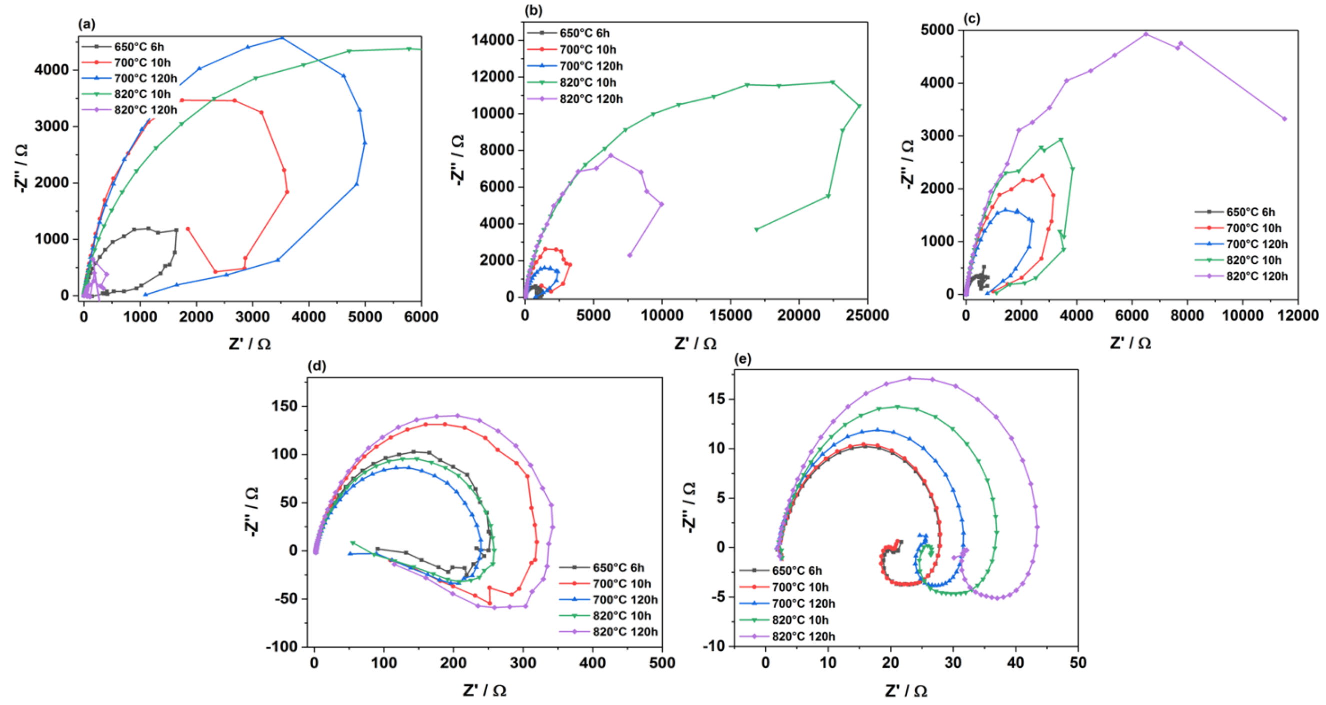

Fig. 4 Nyquist diagram of the EIS test of all the samples at different potentials in the passive-transpassive transition region (a) 800 mV (b) 900 mV (c) 1000 mV (d) 1100 mV (e) 1200 mV

At all potentials, except at 1100 mV, the R_{ct} values do not correlate with the DOS values. At 800 mV, 900 mV, 1000 mV, and 1200 mV, the diameter of the semi-circle in the Nyquist plots are not in tandem with that of the IGC values. The sample heat treated at 700°C for 120 h has a higher DOS and it should show a smaller semi-circle in the Nyquist plots.

However, for EIS measurements at 800 mV, 900 mV, 1000 mV, 1200 mV, this is not observed. Even in the case of samples that are heat treated at the same temperatures for different time periods, no correlation is observed. As mentioned above, this is because only scanning at the DC potential of 1100 mV measures intergranular corrosion.

According to the DOS values from the DL-EPR tests, the sample 700 °C/120 h should have the lowest R_{ct} of all the samples measured at 1100 mV. However, this trend has not been observed. As can be seen in Fig. 4 (d), the sample 650 °C/6 h has a lower R_{ct} than the sample 700 °C/10 h. However, the heat treatment conditions at constant temperature, do follow the trend in relation to DOS values. In Fig. 4 (d), the R_{ct} value of the sample 700 °C/120 h is lower than that of the sample 700 °C/10 h. This is also the case at 820°C. Though R_{ct} values could not differentiate samples with different DOS values, it is good in qualitatively identifying the effect of time on DOS for a given temperature.

IV. CONCLUSIONS

- Anodic polarization curves showed the passive-transpassive behavior in all of the samples and also indicated the region to be between 800-1440 mV. However, these curves give no information concerning DOS.
- An increase in the DC potential for the EIS test, leads to a decrease in R_{ct} due to a transition from passive to transpassive behavior.
- Three regions are identified in the EIS responses: 1) where the dissolution of passive layer takes place (800-1000 mV), 2) where the dissolution of Cr depleted regions takes place (1100 mV) and 3) where pitting corrosion takes place (1200 mV).
- Based on the Nyquist plots and R_{ct} values, it is possible to qualitatively see the influence of heat treatment time on DOS at a given temperature, but not to see the effect of heat treatment temperature.

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