

## The Effects of Cryogenic Treatment on the Corrosion of AISI D3 Steel

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Received: November 11, 2014; Revised: April 24, 2015

It is well known that cryogenic treatment is used to improve the mechanical properties of a material. Consequently, the use of cryogenic treatment has grown beyond its successful application on tool steels. In this research, the effects of cryogenic treatment on the corrosion of AISI D3 steel in 3.5% NaCl solution were examined by electrochemical impedance spectroscopy (EIS). The surface structure of the AISI D3 steel was examined by scanning electron microscopy (SEM) after the EIS investigations. Results clearly indicated that the pre-treatment of the steel was responsible for a significant effect on corrosion. The heat treatment process prior to the cryogenic treatment and the tempering process after were shown to decrease corrosion resistance.

**Keywords:** *corrosion, cryogenic treatment, electrochemical impedance spectroscopy, AISI D3 steel*

### 1. Introduction

Cryogenic treatment is a supplementary process for conventional heat treatment. Unlike mere surface treatments, it is an inexpensive one-time treatment that affects the core properties of the component. Research has shown that cryogenic treatment increases product life and, in most cases, provides additional qualities to the product, such as stress relief and dimensional stability<sup>1,2</sup>. According to previous studies in the literature, two metallurgical phenomena have been reported as the main reasons for using cryogenic treatment: (1) the elimination of retained austenite and (2) the initiation of nucleation sites for the subsequent precipitation of a large number of very fine carbide particles along with their uniform distribution<sup>3,4</sup>. Cryogenically treated samples have also shown a nearly 0% fraction of retained austenite. This means that cryogenic treatment results in the transformation of retained austenite to martensite, which in quenched samples can be as much as 25% in volume. Cryogenic treatment, if properly employed, can provide a significant improvement in both productivity and product quality, and thus, overall machining economy, even after covering the additional cost of the cryogenic treatment<sup>5</sup>.

The alloy AISI D3 is a high-carbon, high-chromium steel developed for various applications which require high resistance to wear, severe pressure and abrasion. These include punching, blanking, stamping, cold-forming dies, cold trimmer and burnishing dies or rolls, slitting cutters, etc. It is worthy to note that punches which are made of AISI D3-grade alloy tool steel contain primarily martensite and metal alloy carbides. Such grades are generally considered to maintain a good balance between wear and corrosion resistance together with dimensional stability.

Corrosion is the continuous gradual destruction of a material due to a chemical reaction with its environment. Corrosion can cause factory shutdowns, waste of valuable resources, loss or contamination of products, reduction in efficiency, costly maintenance, and expensive overdesign. Numerous experimental studies have been carried out to investigate the effect of deep cryogenic heat treatment on the mechanical properties of tool steels; however, very little research has focused on the effect of deep cryogenic heat treatment on the corrosion response<sup>6-8</sup>. The results of the present study showed that, due to a more uniform carbide distribution in association with a higher carbide percentage, the corrosion behaviour of deep cryogenically treated samples had been enhanced. For longer holding durations (e.g., 48 h), the corrosion resistance has been seen to improve as a result of the increase in the carbide percentage by 3% (vol.%) and a more uniform carbide distribution<sup>9</sup>. In the case of most stainless steels, however, cryogenic treatment causes the formation of martensite, which can improve the mechanical properties, but, unfortunately, can also negate the good resistance to corrosion. In steels, martensite is more susceptible to corrosion than austenite. In the deformed samples of the present study, it was found that the precipitated intergranular carbides were always within the martensite or along the martensite lath boundaries. The rapid sensitisation of austenitic steel is due to the fact that chromium and carbon diffuse more rapidly in body-centred-tetragonal martensite than in face-centred-cubic austenite<sup>10</sup>; the corrosion pitting phenomenon tends to initiate from the inclusion-matrix interface and martensite-rich regions. Thus, the objective of this study was to investigate the influences of deep cryogenic treatment and tempering on the corrosion performance of AISI D3 tool steel punches used for blanking on AISI 304 austenitic stainless steel.

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## 2. Material and Methods

Electrochemical measurements were carried out in a three-electrode type cell with separate compartments for the reference electrode (Ag/AgCl), the counter (Pt) and the working (AISI D3 steel) electrodes having an area of 0.5 cm<sup>2</sup>. The surfaces of the working electrode were prepared by grinding with 400-1800 grade abrasive paper, rinsing with distilled water and then degreasing with acetone. During the measurements, the solution was stirred with a magnetic stirrer (500 rot/min). The composition of AISI D3 steel is given in Table 1.

Four types of uncoated AISI D3 steel samples were used: conventionally heat treated, 24 h cryogenically treated, 36 h cryogenically treated and 36 h cryogenically treated and then 2 h tempered at 150 °C. The cryogenic treatment for the AISI D3 samples was achieved by gradually lowering them from room temperature to -145 °C at the cooling rate of about 5 °C/min and holding at this cryogenic temperature for 24 h or 36 h, then gradually bringing them back to room temperature at the heating rate of 5 °C/min. The scheme in Figure 1 shows the various treatments and treatment cycles applied to the samples. The tempering of the AISI D3 steel was performed in a muffle furnace with the capacity of 9 kW, 380 V and 1200 °C.

**Table 1.** Chemical composition of AISI D3 steel.

Element	Amount (wt %)
Carbon	2.0-2.3
Manganese	0.6
Silicon	0.6
Nickel	0.30
Chromium	11.0-13.5
Sulphur	0.03
Phosphorus	0.03
Vanadium	1.0
Ferrous	Remainder

After the AISI D3 steel samples were prepared as described above (Figure 1), their corrosion behaviour in a 3.5% NaCl medium was then examined. For the investigation, abridged labels were used for the AISI D3 steel sample qualifications (Table 2). Thus, the following discussion will be made easier by referring to these codes.

### 2.1. Electrochemical measurements

The electrochemical impedance spectroscopy (EIS) measurements were performed using a Reference 600 Gamry Potentiostat/Galvanostat/ZRA (M/S Gamry Instruments, USA). Before EIS measurement, each sample was immersed in the corrosion cell and allowed to stabilise for 2 h. The EIS studies were performed by imposing a sinusoidal voltage of 10 mV amplitude as the open circuit potential of the working electrode. The frequency was varied between 100 kHz and 1 mHz.

### 2.2. Surface morphology studies

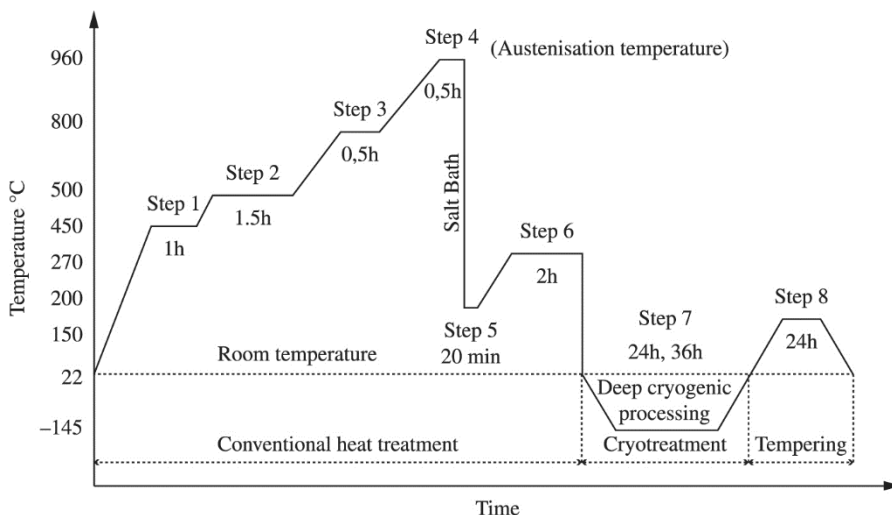
After the EIS measurements, surface analyses of the working electrodes were carried out by scanning electron microscopy (SEM) using the Quanta FEG 250 (FEI) model equipped with an energy-dispersive X-ray spectroscopy (EDS) probe.

## 3. Results

### 3.1. Electrochemical Impedance Spectroscopy (EIS)

The corrosion behaviour (in the 3.5% NaCl medium) of the AISI D3 steel samples prepared with different pre-treatments was investigated by means of EIS conducted at room temperature. The Nyquist, Bode and phase angle plots of the steel alloy are shown in Figures 2 and 3.

As shown in Figure 2, the impedance diagrams take the form of depressed semicircles, indicating charge transfer and diffusion processes. Similar depressed semicircles were



**Figure 1.** A schematic presentation of the heat treatment schedule consisting of the hardening, deep cryogenic treatment and tempering cycles of the samples.

obtained with a single time constant, due to the surface heterogeneity of the corrosion product covering the surface at random sites<sup>11-14</sup>. The corresponding Bode plots are shown in Figure 3a. All these findings demonstrate that the investigated AISI D3 steel alloy samples exhibited similar corrosion mechanisms in the 3.5% NaCl solution.

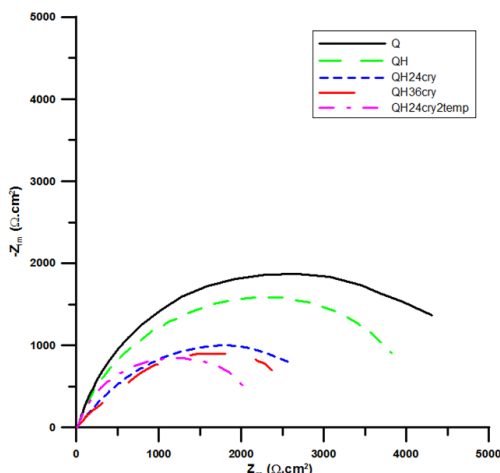
The Nyquist plots, analysed with the ZSimpwin 3.10 programme, provide accurate information about the

circuit. The measure of goodness-of-fit of the model is the  $\chi^2$  parameter. During the analysis,  $\chi^2$  did not exceed  $1 \times 10^{-4}$ , attesting to a very high fit of the received impedance spectra to the proposed electrical equivalent circuit<sup>15</sup>.

It is clear from previous research and the applied ZSimpwin 3.10 programme that the obtained Nyquist plots can be modelled by a simple Randel's circuit including the charge transfer resistance ( $R_{ct}$ ) parallel with double-layer capacitance ( $C_{dl}$ ) in series with solution resistance ( $R_s$ )<sup>16</sup>. However, Figure 2 shows that the Nyquist plots of AISI D3 steel in 3.5% NaCl were not the perfect semicircles expected from the EIS assumption. This difference can be explained by the non-ideal behaviour of the double layer as a capacitor. Therefore, it was necessary to use a constant phase element, CPE ( $Q$ ), instead of a double-layer capacity to account for the non-ideal behaviour<sup>17</sup>. Consequently, the  $R(Q)R$  circuit model was used to analyse the EIS results<sup>18</sup>. The impedance parameters derived from these investigations are given in Table 3. The impedance of the CPE can be described by Equation 1:

**Table 2.** Investigated AISI D3 steel sample codes and qualifications.

Sample (AISI D3) Code	Qualifications
Q	Without pre-treatment
QH	Heat treatment
QH24cry	Heat treatment + 24 h cryogenic treatment
QH36cry	Heat treatment + 36 h cryogenic treatment
QH36cry2temp	Heat treatment + 36 h cryogenic treatment + 2 h tempered

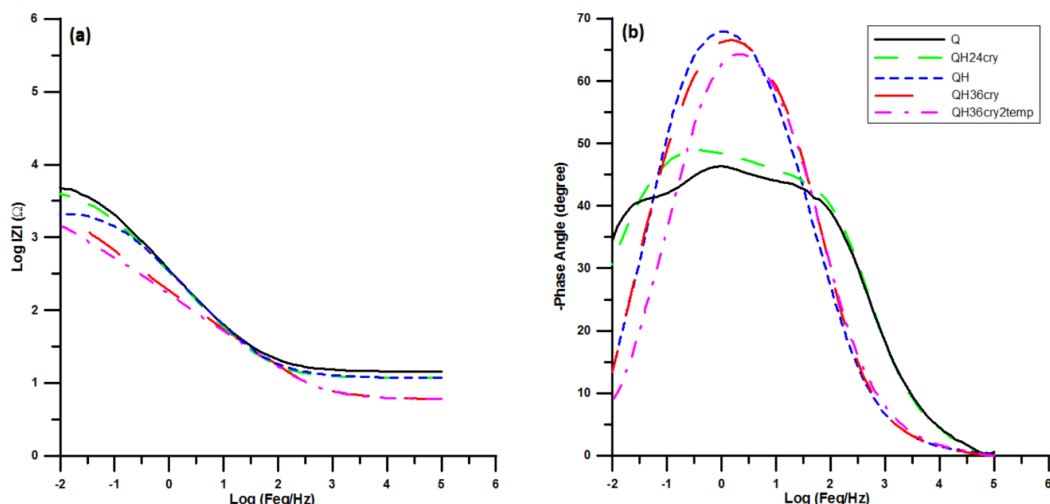


**Figure 2.** EIS data represented by Nyquist diagrams for different pre-treated AISI D3 steel samples in 3.5% NaCl solution.

$$Z_{CPE} = [Y_0(j\omega)^n]^{-1} \tag{1}$$

According to this formula, the CPE element may be considered as a double-layer capacitor only when the  $n$  values remain close to 1. The  $n$  parameter obtained by means of this study ranged from 0.54 up to 0.80, thus fulfilling the above requirement. It is noticeable that an increase in  $Q$  values is associated with a decrease in  $n$  values. Moreover, Table 3 shows that all applied pre-treatment processes caused an increase in their respective  $Q$  values.

Figure 3b gives phase angle vs. log frequency changes according to the pre-treatment of the AISI D3 steel samples in 3.5% NaCl solution. The phase angle values are appropriate for the  $R_{ct}$  changes. The heat, cryogenic and tempering pre-treatment processes decreased the phase angle from 35 to 9 degrees. The calculated  $R_{ct}$  values also decreased with all pre-treatment procedures. It is recognised in previous research that temperature plays an important role in the



**Figure 3.** EIS data represented by Bode (a) and phase angle (b) variation vs. log frequency diagrams for different pre-treated AISI D3 steel samples in 3.5% NaCl solution

progress of corrosion reactions and that heat pre-treatment increases the corrosion rate<sup>19,20</sup>. The changes in  $Q$  and  $n$  values confirmed these findings. The  $R_s$  values were between 9 and 14  $\Omega$  and nearly constant, as expected, because the solution was the same for all samples.

### 3.2. Morphological measurements

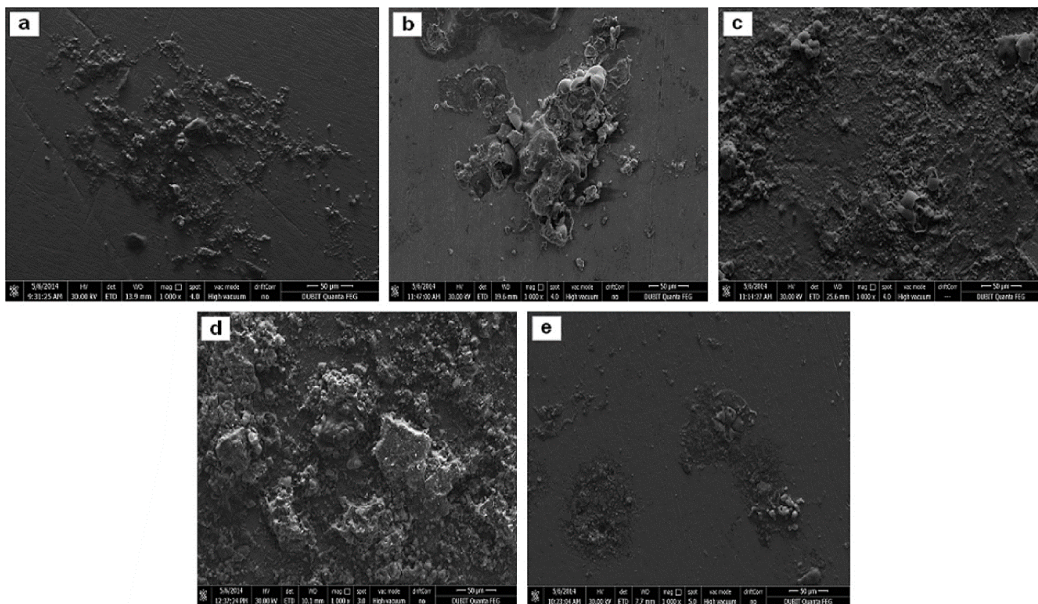
EDS results were obtained from averages of the entire surface areas of the presented SEM images. The SEM micrographs are shown in Figure 4a-e. Table 4 gives the corresponding EDS spectra of the surface of the AISI D3 steel specimens after conducting electrochemical tests (EIS) on the different pre-treated samples in 3.5% NaCl solution. Figure 4a-e reveals that the pre-treatment of AISI D3 steel had a significant effect on the corrosion process. It is clear from Figure 4 that the surface of (a) was damaged less than the others (b-e). The surface of sample (e), with

heat treatment + 36 h cryogenic treatment + 2 h tempering, was damaged by pitted areas in the typical form of pitting corrosion<sup>21,22</sup>. The surface roughness of samples (d) and (c) seemed to be greater than that in the other SEM images. This study also suggests that initial surface roughness does not have a predominant effect on corrosion resistance. Rather, corrosion resistance is associated with both compressive and residual stresses<sup>23</sup>.

Table 4 shows the general EDS analysis results of the samples and their concentrations (wt%). Based on the corresponding EDS results, it can be concluded that all AISI D3 steel samples were corroded in the 3.5% NaCl solution. These findings validate the SEM and EIS results. While the concentration of C was mostly constant, O, Cr and Mn concentrations increased depending on the type of pre-treatment. The reduction in the amount of Fe and the increase of Cr has also been reported in previous studies<sup>24</sup>.

**Table 3.** Impedance parameters for different pre-treated AISI D3 steel samples in 3.5% NaCl solution

Metal	$R_s$ ( $\Omega$ )	$Q$ (CPE)	$n$ ( $0 \leq n \leq 1$ )	$R_{ct}$ ( $\Omega$ )	$\chi^2$
Q	13.72	3.69E-04	0.80	5522	1.91E-04
QH	8.687	8.53E-04	0.68	4518	1.99E-04
QH24cry	9.292	1.16E-03	0.59	3490	2.57E-05
QH36cry	10.34	1.56E-03	0.55	2839	3.03E-04
QH36cry2temp	12.06	1.78E-03	0.54	2354	6.80E-04



**Figure 4.** SEM images for different pre-treatment AISI D3 steel samples in 3.5% NaCl solution: (a) Q, (b) QH, (c) QH24cry, (d) QH36cry, (e) QH36cry2temp

**Table 4.** General EDS results of concentration (wt%) of samples (a-e) in Figure 4.

Element	General EDS results of Figure 4 samples (a-e) conc. (wt%)				
	Q	QH	QH24cry	QH36cry	QH36cry2temp
C	3.19	2.67	3.12	3.49	3.75
O	25.28	31.67	35.47	41.06	45.52
Cr	7.47	10.01	10.45	10.92	11.7
Mn	0.3	0.36	0.34	0.35	0.42
Fe	63.76	55.29	50.62	44.18	38.61

## 4. Conclusions

1. The values of the EIS, SEM and EDS results were in good agreement with each other. The combination of these techniques demonstrated a powerful approach in defining the corrosion process.
2. All investigated samples were corroded in 3.5% NaCl. Furthermore, the corrosion resistance of these samples can be ranked as follows: Q > QH > QH24cry > QH36cry > QH36cry2temp.
3. In contrast to the other samples, pits occurred on the surface of the sample of QH36cry2temp pre-treated

AISI D3 steel in 3.5% NaCl, indicating that the pre-treatment procedure had changed the microstructure of the alloy.

4. The use of cryogenic treatment is steadily gaining acceptance as a process for improving the mechanical behaviour of steels. However, as it is well known that corrosion is an electrochemical process, the data obtained here may not be valid for this orientation. Despite the relevant results presented in this study, more detailed knowledge of the process mechanisms under investigation may be provided by utilising DEIS, AES, XPS, Tofu-SIMS and cross-sectional TEM in future studies.

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