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The Effect of Heat Treatment on the Corrosion Resistance of 440C Stainless Steel in 20% HNO_3 + 2.5% $Na_2Cr_2O_7$ Solution

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The effect of heat treatment on the corrosion resistance of 440C stainless steel was investigated in a 20% HNO_3 + 2.5% $Na_2Cr_2O_7$ solution using electrochemical noise (ECN) measurements, electrochemical impedance spectroscopy (EIS), and scanning electron microscopy (SEM) examinations. The noise resistance (*R*n), which has been found to be inversely related to the localized corrosion rate, was measured to be 5.7E + 08 Ω-cm^2, 4.2E + 08 Ω-cm^2, and 3.7E + 04 Ω-cm^2 for the oil-quenched, air-quenched, and vacuum furnace cooled (VFC) samples, respectively, after 1200 s exposures. The *R*n for all heat treat conditions stabilized within a range of 1.0E + 07 Ω-cm^2 to 3.2E + 08 Ω-cm^2 after 2 h exposures. The EIS response showed a polarization resistance (*R*p) on the order of 6.6E + 04 Ω-cm^2, 5.3E + 04 Ω-cm^2, and 1.1E + 04 Ω-cm^2 for the oil-quenched, air-quenched, and VFC samples, respectively, after 2 h exposures. The EIS data are in good agreement with ECN data and indicate that after longer exposures, general corrosion mechanisms dominate and the corrosion rates are comparable. SEM examinations of specimens subjected to 1200 s exposures revealed that severity of pitting and intergranular corrosion damage was consistent with trends in the *R*n data. Specifically, the electrochemical noise data as well as SEM examinations of specimens revealed a higher localized corrosion resistance of the hardened specimens during the early stages of passivation. This greater resistance to localized corrosion can be attributed to an increased stability of the natural passive film resulting from a higher concentration of chromium atoms in solution for the martensite phase.

Keywords air quench, AISI 440C, corrosion, electrochemical impedance spectroscopy, hardness, heat treating, hydraulic control valves, martensitic stainless steel, nitric acid noise resistance, oil quench, passivation, pitting corrosion, polarization resistance, scanning electron microscopy

1. Introduction

AISI Type 440C belongs to a category of high-carbon high-chromium martensitic stainless steels commonly used in the aerospace industry for hydraulic control valve assemblies. Important material properties for these applications include moderate corrosion resistance, high wear resistance, and dimensional stability. The controlling heat treatment specification for 440C requires that parts with a section thickness exceeding 0.635 cm (0.25 in.) are oil or polymer quenched from the austenitizing temperature.[1] However, for typical control valve slide and sleeve parts that contain high length-to-diameter ratios and frequent changes in section thickness, oil quenching results in excessive dimensional distortion and increased susceptibility to quench cracking. Parts with excessive heat treat distortion are required to go through a full annealing process, followed by straightening and stress relieving operations, and a complete re-heat treatment cycle. Post-heat treatment straightening operations have been considered for this application and have been ruled out for several reasons. For example, hot straightening requires heating above the tempering temperature of 191 °C (375 °F). Room temperature (RT) straightening in the fully hardened condition is avoided due to the possibility of inducing high residual stresses, cracks, or brittle fracture. Post-heat treat straightening operations, in general, are costly and operator dependent, and if not properly controlled may allow for subsequent dimensional changes.

Air quenching is used in the current study to quantify dimensional distortion compared with oil quenching for a standard valve sleeve heat treat blank as illustrated in Fig.1 (several detail dimensions are omitted for clarity). This part geometry represents the largest of a family of control valve sleeve heat treat blanks used for hydraulic applications and is rough machined from bar stock as shown, to minimize more costly grinding operations in the hardened condition. Air quenching tests yielded satisfactory dimensional control, less than half of the distortion caused by oil quenching, and acceptable section hardness. This process was repeated on several parts to ensure data reproducibility. There are concerns, however, that a slower quench rate can cause a decrease in corrosion resistance. For hydraulic applications, corrosion resistance is most important during the post-heat treatment machining processes where parts are exposed to various water-based cleaning cycles and a final nitric acid passivation treatment. In application, the parts are coated with hydraulic fluid that inhibits corrosion. However, if pitting and intergranular corrosion go undetected

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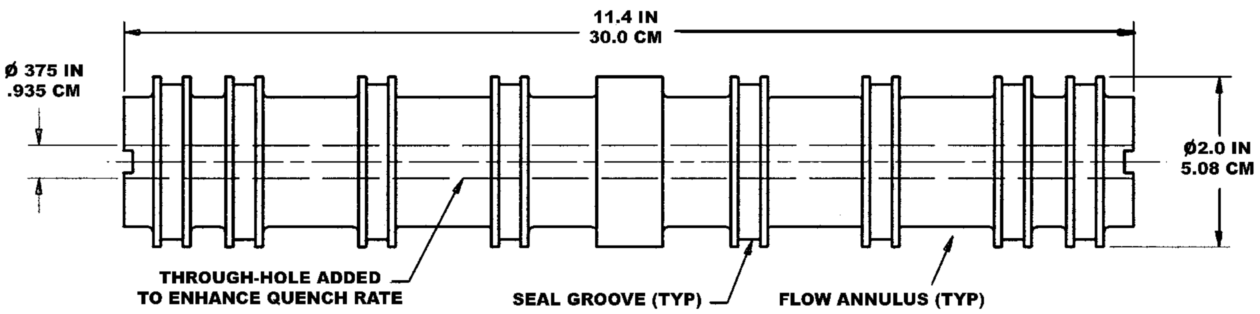

Fig. 1 Valve blank illustrating features that are rough machined prior to heat treatment. Note the center 0.035 cm (0.375 in) diameter hole is electrical discharge machined to larger 2.54 cm (1.0 in.) diameter after heat treatment to accommodate a valve slide element

during the fabrication cycle, of a severity that can compromise design margins, this damage can lead to fatigue crack initiation or unstable brittle fracture in acceptance testing or service. The controlling passivation specification does suggest that 440C is susceptible to intergranular corrosion, and thus, alternate chemical and mechanical cleaning methods are preferred.[2] However, mechanical methods are more costly and impractical when the part geometry becomes complex. Other chemical means such as alkaline cleaners are not as effective for dissolving iron particles and other surface contaminants embedded during fabrication.

A literature review was conducted, focused specifically on the corrosion properties of 440C. An attempt was made to better understand the effects of quench rate on corrosion resistance. ASM International has published several resources to aid in the selection of heat treatment cycles for a specific alloy and design application. In general, these references suggest that due to the high hardenability associated with martensitic stainless steels, they can be quenched in either air or oil. However, they also imply that although air quenching may be required for large or complex sections to prevent distortion or quench cracking, a decrease in corrosion resistance may occur.[3-5] These references indicate that oil quenching will provide optimum corrosion resistance, but the differences are not quantified.

Sheasby and Walzak[6,7] did investigate the specific effects of austenitizing temperature and quench rate on the stability of 440C passive films. It was reported that variations in the austenitizing temperature and quenching rate did directly impact the stability of the natural passive film. Different heat treat processes were used on 440C samples and they were characterized with regard to their open circuit voltage decay in a 0.075 M H_2SO_4 solution from an electrically passivated state. For example, samples that were austenitized in the range of 1065-1100 °C (1950-2012 °F) and quenched at a rate of 25-30 °C/s (45-54 °F/s) demonstrated proper film stability as determined by their stabilized potentials. In contrast, parts that were austenitized in the range of 950-1000 °C (1742-1832 °F) and quenched at a rate of 5-25 °C/s (9-45 °F/s), stabilized below a threshold potential where corrosion attack at prior austenite grain boundaries and carbide particles was reported.

The current study is designed to better understand the effect of quench rate on the localized corrosion processes that occur with type 440C alloy in a standard nitric acid plus sodium dichromate passivation solution. Of particular interest is any difference in the localized (pitting and intergranular) corrosion resistance for the oil- and air-quenched conditions. The corrosion processes are quantified using electrochemical noise (ECN) measurements and electrochemical impedance spectroscopy (EIS). The noise resistance (*R*n), found to be inversely related to the localized corrosion rate, is measured for each heat treat condition and is computed by taking a ratio of the standard deviations of the potential and coupling current during specific block exposure times.[8-10] A low value of *R*n indicates frequent fluctuations in current, thus signifying a high incidence of localized corrosion processes. EIS is also used to investigate the corrosion processes and to measure the polarization resistance (*R*p) of the various heat treat conditions. The value of the *R*p is generally considered inversely proportional to the corrosion rate and in many cases, as with the *R*n, is used along with the Stern-Geary relationship to compute corrosion rates.[10] Further details of the EIS technique can be found in recent publications.[11,12] Note that the vacuum furnace cooled (VFC) specimens were used strictly as a baseline for comparison to the hardened specimens, with the anticipated corrosion resistance being much lower.

2. Experimental Procedure

2.1 Materials and Heat Treatments

The raw material used for the current study is designated as AISI Type 440C (UNS S44004) and was procured per the Aerospace Materials Specification (AMS) 5618F.[13] Table 1 lists the alloy chemistry requirements for this specification and the composition for the heat lot used in the present investigation. The as-received material was 6.35 cm (2.50 in.) diameter bar stock in the VFC condition with hardness of 253 HB. To obtain the VFC condition, the material was heated to 871 °C (1600 °F) for 1 h, furnace cooled to 790 °C (1450 °F), and cooled at a rate of 20 °C/h (36 °F/h) to 595 °C (1100 °F), followed by air cooling to RT. The heat treat blanks were prepared with a 20.32 cm (8.0 in.) length by 5.72 cm (2.25 in.) diameter with a 1.9 cm (0.75 in.) diameter by 5.08 cm (2.0 in.) depth cavity drilled at the ends to accommodate thermocouple sensors during the heat treatment cycles. Thus, the cooling rates measured were more indicative of the core (slower) cooling rates. The heat treat blanks for the corrosion experiments were designed to simulate a worst-case valve heat treatment blank geometry in terms of maximum section thickness and weight. For example, when compared with the valve heat treatment blank illustrated in Fig. 1, the blanks for the corrosion experiments did not include any rough machining on the part outer diameter or a through-hole down the center, both of which increase quench rate and, therefore, hardness.

The oil-quenched blank was heat treated strictly to the AMS 2759[1] and was subjected to the following thermal treatments: (1) preheated in a vacuum to 649 °C (1400 °F) for 30 min; (2) austenitized in a vacuum at 1052 °C (1925 °F) for 1 h; (3) oil bath quenched to 54 °C (130 °F) and stabilized to RT; (4) cold stabilized in liquid nitrogen at −73 °C (−100 °F) for 2 h; (5) tempered at 191 °C (375 °F) for a 2 h duration, followed by air cooling; and (6) final tempered at 191 °C (375 °F) for a 2 h duration followed by air cooling. The air-quenched blank was treated exactly as above except the oil quench was replaced with an air quench. In each case, the blanks were heat treated with a typical production load size of 90-140 kg (200-300 lbs) and were nestled in the center of several representative pieces of steel.

The actual time-temperature histories for the air and oil quenching of the heat treat blanks are illustrated in Fig. 2 on a Time-Temperature-Transformation (TTT) plot for the 440C composition. The air quench data in Fig. 2 show a slight intersection with the nose of the transformation curve that was not considered to be an issue with regard to the overall mechanical properties as long as the needed section hardness was achieved. In practice, a minimum HRC value of 56 is normally specified. The section hardness values produced after final tempering are provided in Fig. 3 for the respective heat treat cycles. For comparison, also shown are the section hardness values for the valve heat treatment blanks illustrated in Fig. 1 that were used to evaluate dimensional distortion. These hardness values, as expected, are slightly higher due to the enhanced cooling rate associated with the rough machining. The main focus of this study was to compare the corrosion behaviors resulting from the different heat treatments. As previously mentioned, the corrosion experiments also included evaluation of a VFC condition, primarily to act as a baseline for comparison to the hardened material.

2.2 Specimen Preparation

Specimens were prepared for both the ECN and EIS measurements as required for installation into their respective corrosion test cells. The ECN specimens consisted of small bars with a 5.08 cm (2.0 in.) length by 0.635 cm (0.25 in.) diameter that were extracted from the center section of the 5.72 cm (2.25 in.) diameter heat treated blanks requiring a wire electrical discharge machining (EDM) process due to the high hardness. The EIS test cell required wafer-shaped specimens that were extracted from heat treated bars using an EDM process. These bars consisted of an outside diameter of 5.72 cm (2.25 in.) and a thickness of 0.254 cm (0.100 in.). In each case, the specimen surfaces were then finished by low stress grinding: removing all re-cast layers and then polishing by a 600 grit sandpaper.

Table 1 Alloy Chemistry Ranges (wt.%) for Type 440C Stainless Steel per AMS5618 and Actual Values for the Heat Lot Used in the Present Investigation

Alloy Type	C	Mn	Si	P	S	Cr	Mo	Ni	Cu
440C per AMS5618[13]	0.95/ 1.20	1.00 max	1.00 max	0.020 max	0.010 max	16.0/ 18.0	0.40/ 0.65	0.75 max	0.50 max
440C per present investigation	1.06	0.52	0.33	0.019	0.006	16.8	0.49	0.17	0.05

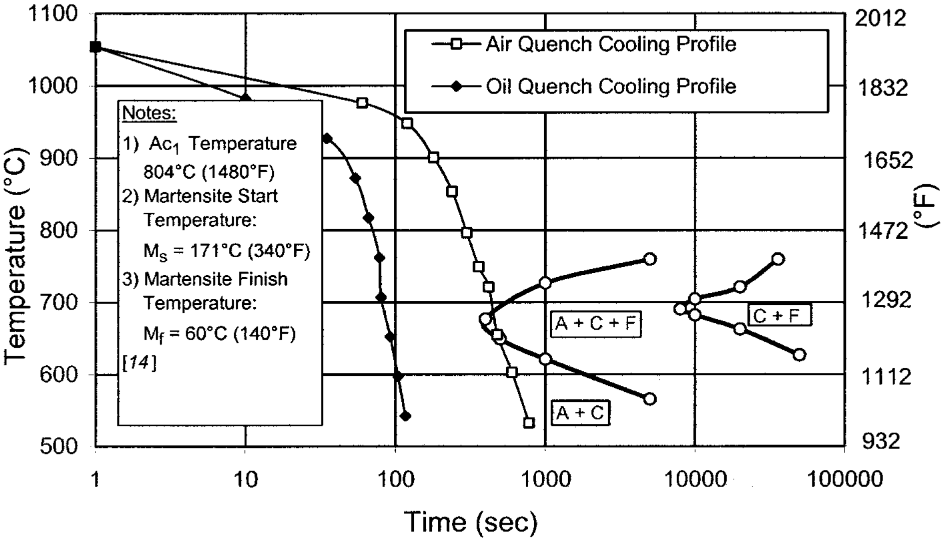

Fig. 2 Air- and oil-quench cooling profiles for 440C heat treatment blanks vs TTT plot for Type 440C stainless steel (data provided courtesy of Carpenter Steel Co., Wyomissing, PA)

The corrosion specimens were stored in corrosive preventative oil until ready for use. Just prior to each of the experiments, the specimens were ultrasonically cleaned in acetone, water rinsed in distilled water, and air-dried.

2.3 Corrosion Test Cells

The corrosion test cells used for the ECN and EIS measurements are illustrated in Fig. 4 and 5, respectively. The test cells were of similar construction and allowed for elevated temperature testing by use of metal heating filaments around the chamber circumference. All experiments were conducted in a solution consisting of 20% (by weight) nitric acid (HNO_3) + 2.5% (by weight) sodium dichromate ($Na_2Cr_2O_7$) maintained at 54 °C (125 °F). This solution type, concentration, and temperature replicates the type used for passivation treatments of these components during the manufacturing process.[2] The test cells were equipped with a standard silver-silver-chloride reference electrode and contained Teflon plates below and above the cells for electrical insulation.

For the noise measurements, both the working and counter electrodes consisted of 440C alloy (the material under investigation) and the ends were mounted flush to the inside diameter of the test cell leaving 0.317 cm^2 (0.049 $in.^2$) in contact with the solution. An epoxy compound was used to seal the outside surfaces of the electrodes. Special caution was used to

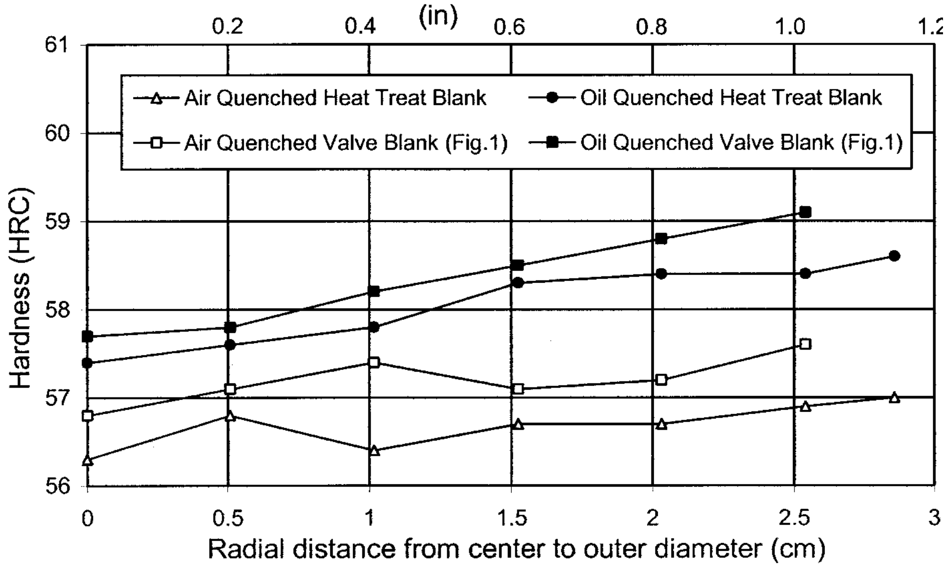

Fig. 3 Hardness traverse results for air- and oil-quenched heat treatment blanks used for corrosion experiments and for valve heat treat blanks (illustrated in Fig. 1) used for the heat treatment distortion studies

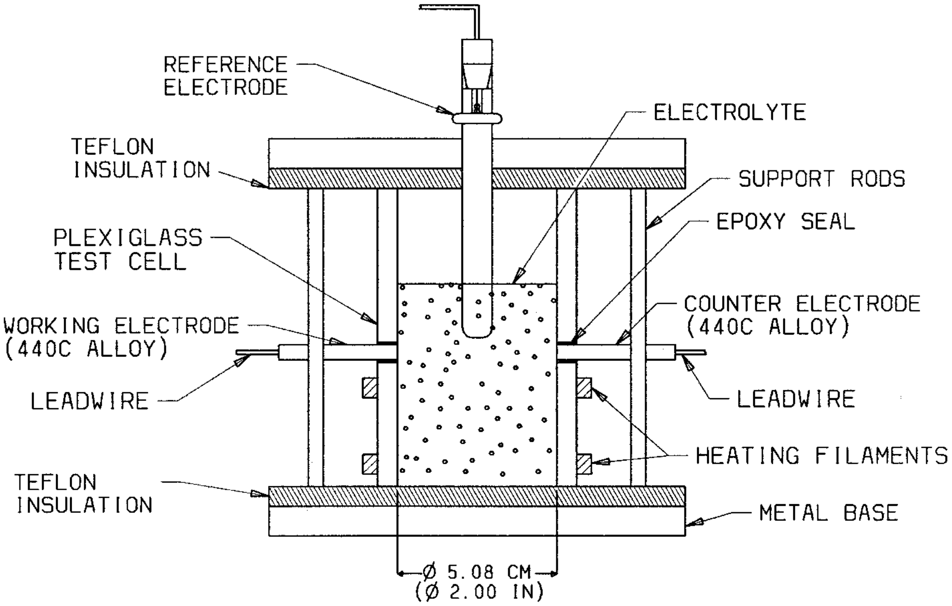

Fig. 4 Schematic representation of corrosion test cell used for the ECN measurements

avoid porosity or crevices in the epoxy that could result in the solution leaking or in crevice corrosion of the samples.

For the impedance measurements, the working electrode was 440C alloy and the counter electrode was commercially pure titanium. The working electrode under investigation is placed at the bottom of the glass cylinder chamber, leaving 20.3 cm^2 (3.14 in.^{2}) in contact with the solution. The counter electrode was positioned roughly 2.54 cm (1.0 in.) above the working electrode. The bottom of the test cell contained an O-ring for sealing that did need replacement on occasion due the deterioration from the acid medium.

2.4 Electrochemical Measurements

Electrochemical measurements were performed using a Solartron-Schlumberger (Solartron Group, Farnborough, Hampshire, UK) electrochemical measurement unit (SI 1280) connected to a desktop computer. The program that controls the SI 1280 instrument and records the readings was developed inhouse using the Labview (National Instruments Corp., Austin, TX) graphical programming language. The electrochemical noise readings, consisting of a ratio of the working electrode's standard deviations of potential and current, were based on a sampling frequency of 4 Hz and a sampling block time of 1200 s. The noise measurements were taken immediately after the addition of the medium. The electrochemical impedance measurements were made at the open circuit potential using a ±10 mV amplitude ac potential over frequencies ranging from 20 000-0.001 Hz after an approximate 2 h exposure.

3. Results and Discussion

Figure 6 illustrates the *R*n versus time for the three heat treat conditions. Of most interest for the present investigation are the *R*n values after 1200 s exposure time. This exposure time simulates the passivation treatment used in fabrication. The *R*n values after the 1200 s exposure were measured to be 5.7E + 08 Ω-cm^2, 4.2E + 08 Ω-cm^2, and 3.7E + 04 Ω-cm^2 for the oil-quenched, air-quenched, and VFC samples, respectively. The *R*n for all heat treat conditions stabilized within a range of 1.0E + 07 Ω-cm^2 to 3.2E + 08 Ω-cm^2 after 2 h exposures. As expected, the oil-quenched sample does maintain the highest *R*n, although only slightly higher than the air-quenched sample. Interestingly, the VFC sample's *R*n is roughly four orders of magnitude less than the hardened samples after a 1200 s exposure. This low initial *R*n, followed by a dramatic rise, is attributed to a high degree of localized corrosion initially followed by more general corrosion.

Impedance spectra for the three heat treat conditions are illustrated in Fig. 7. These data exhibit a smooth, single time constant response. The low frequency data plateau corresponds to the sum of the *R*p and the solution resistance. The high frequency plateau represents the solution resistance only. The value of *R*p was determined to be 6.6E + 04 Ω-cm^2, 5.3E + 04 Ω-cm^2, and 1.1E + 04 Ω-cm^2 for the oil-quenched, air-quenched, and VFC samples, respectively, after an approximate 2 h exposure. The low frequency data indicate the *R*p of the air- and oil-quenched samples are about the same. The difference in *R*p between the VFC and hardened samples is less than an order of magnitude. Since the test duration for the EIS measurements is based on longer exposure times, for example, compared with the initial 1200 s exposure for the noise measurements, the EIS data were not as useful for rating the material's initial corrosion resistance under passivation conditions. Rather, these data indicate relative behaviors after further exposure to a corrosive environment.

Scanning electron micrographs of the oil-quenched, air-quenched, and VFC samples are shown in Fig. 8 (a-c), respec tively, after a 1200 s exposure period. The oil- and air-quenched samples exhibited a similar degree of corrosion damage, predominantly intergranular corrosion with some evidence of pitting. The pitting damage appeared to be at areas where larger carbide particles previously existed. These areas are evidently vulnerable to attack and this can be attributed to a depletion of chromium directly adjacent to these chromium-rich car-

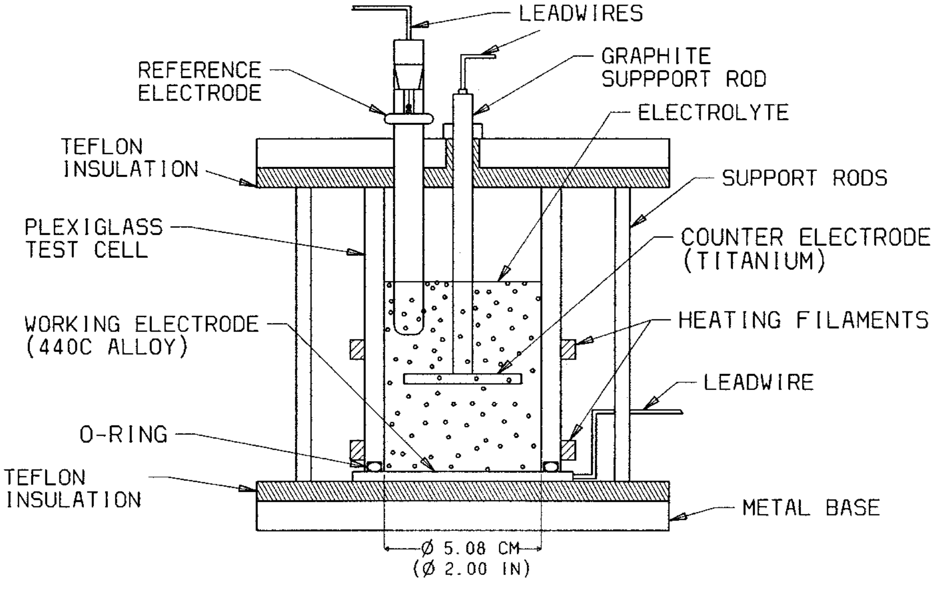

Fig. 5 Schematic representation of corrosion test cell used for the EIS

bides. The VFC sample showed general corrosion along with larger pits, presumably due to the larger carbides.

The results of this study suggest further investigations are in order: for example, using citric acid as opposed to nitric acid for passivation in an attempt to minimize corrosion damage, although there are concerns that citric acid may not be as effective for removing surface contaminants; also, quantifying reductions in fatigue resistance of samples exposed to the degree of corrosion damage consistent with the passivation process.

4. Conclusions

1) Air quenching of type 440C control valve sleeve heat treat blanks (Fig. 1) resulted in less than half the dimensional distortion caused by oil quenching, thus meeting straightness requirements for the present investigation. Acceptable hardness levels were also achieved, specified as HRC 56 minimum.
2) The *R*n of the air- and oil-quenched samples was roughly the same after a 1200 s exposure period in the passivation solution. For longer exposures, in the 1-2 h range, the air-quenched sample's *R*n dropped by a factor of 15, but eventually increased to the level of the oil-quenched sample's *R*n. The *R*n of the VFC sample was roughly four orders of magnitude less than the hardened samples after 1200 s exposure to the passivation solution. This value also increased to the *R*n of the hardened samples after longer exposures, indicating a transition from severe localized corrosion to more general corrosion.
3) The EIS results, representative of 2 h exposure, did not indicate a significant difference in the *R*p between the oil- and air-quenched conditions (Fig. 7). This was in close

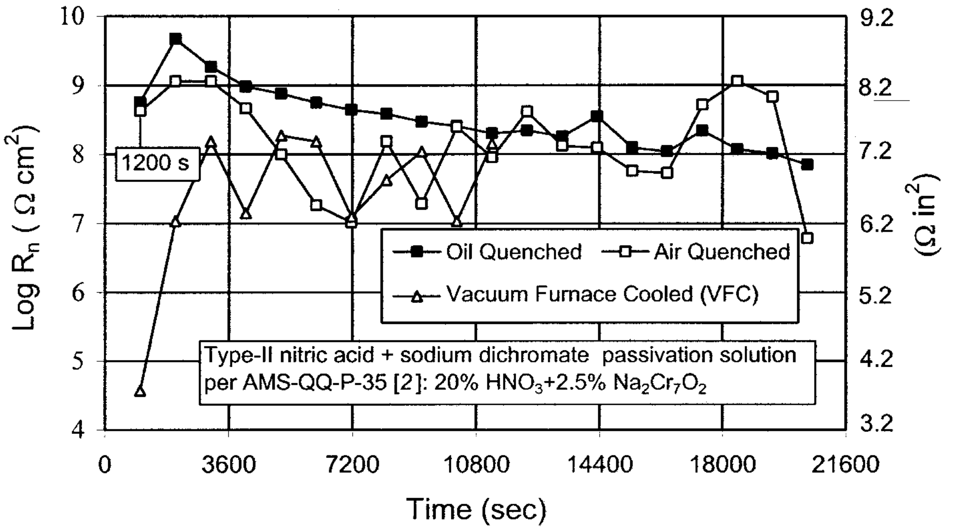

Fig. 6 *R*n vs time for oil-quenched, air-quenched, and VFC Type 440C alloy in a nitric acid passivation solution. Note the negligible difference in *R*n for the oil and air quenched samples after a 1200 s exposure.

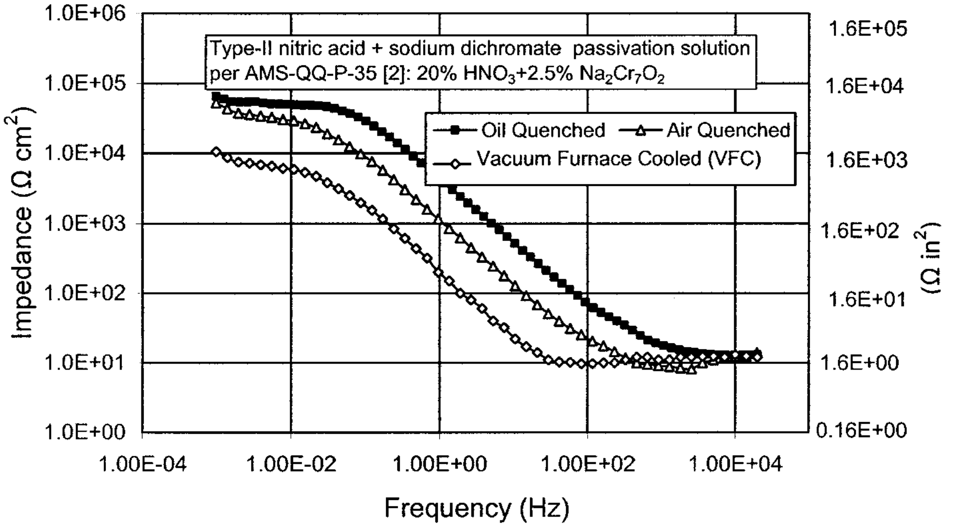

Fig. 7 Electrochemical impedance spectra (Bode plot) for oil-quenched, air-quenched, and VFC Type 440C alloy after 2 h exposure in a nitric acid passivation solution

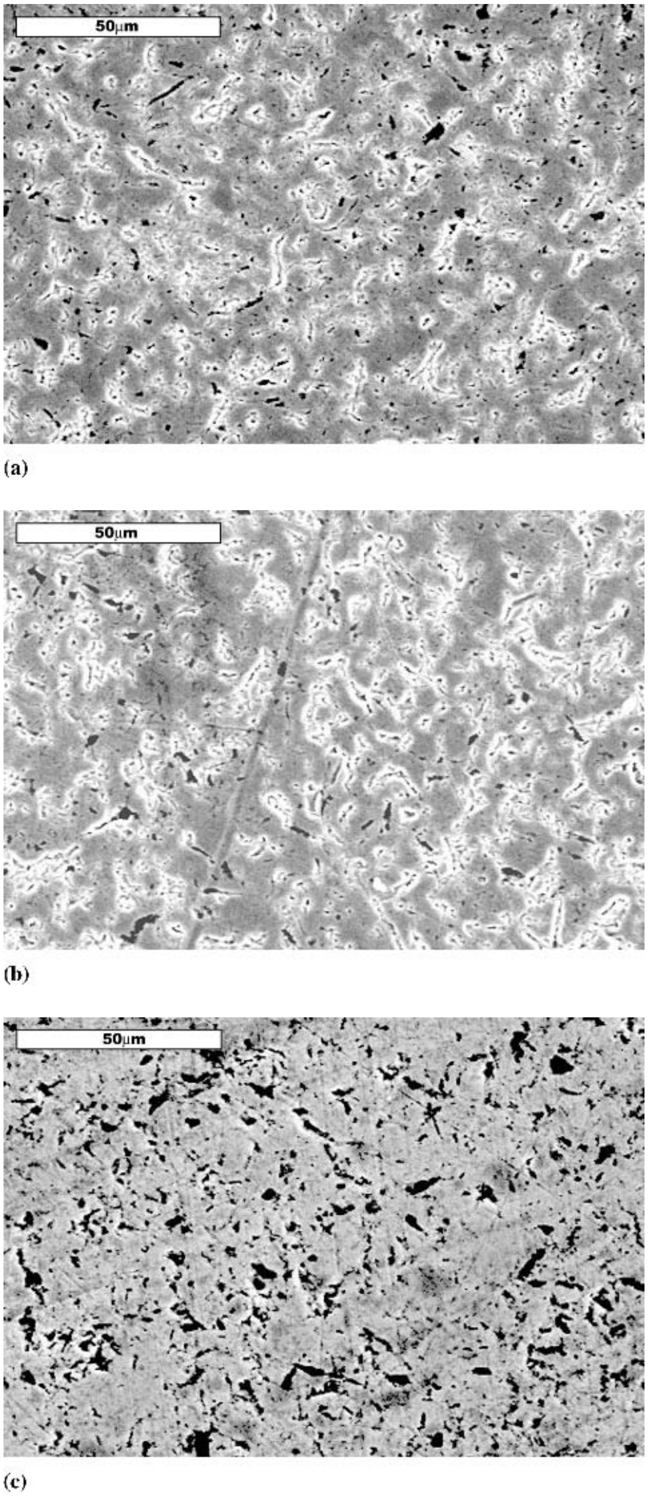

Fig. 8 SEM micrographs at 1000× magnification of corrosion damage for **(a)** oil-quenched; **(b)** air-quenched; and **(c)** VFC Type 440C alloy after 1200 s exposure in a nitric acid solution passivation solution

agreement with the noise resistance data that indicated that the level of localized corrosion is roughly the same for these specimens. A significantly lower value of *R*p for the VFC sample was consistent with the noise data, indicating a greater overall susceptibility to corrosion in harsh environments compared with that for the other samples.

4) SEM examinations of hardened samples subjected to 1200 s exposures revealed both pitting corrosion and intergranular corrosion at prior austenite grain boundaries. The corrosion damage was comparable for the air- and oil-quenched samples. The annealed sample showed more general corrosion damage with somewhat more severe pitting damage (Fig. 8). Thus, the SEM observations were consistent with the electrochemical measurements and indicated an overall greater susceptibility to corrosion for the VFC sample.
5) In general, for the present nitric acid passivation solution,[2] air quenching as opposed to oil quenching does not cause a significant degradation in the localized corrosion resistance after 1200 s or 2 h exposure periods.

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