Impedance of steels in new and degraded ester based lubricating oil

Kerry N. Allahar\(^a\), Darryl P. Butt\(^a\), Mark E. Orazem\(^b\),* , Herbert A. Chin\(^c\), Gene Danko\(^c\), William Ogden\(^c\), Ronald E. Yungk\(^c\)

\(^a\) Department of Materials Science and Engineering, University of Florida, Gainesville, FL 32611, USA
\(^b\) Department of Chemical Engineering, University of Florida, Gainesville, FL 32611, USA
\(^c\) Pratt and Whitney, Materials and Processes Engineering, Mail Stop 114-42, 400 Main St. East Hartford, CT 06108, USA

Received 15 July 2004; received in revised form 16 December 2004; accepted 8 February 2005
Available online 27 October 2005

Abstract

The measurement model technique was used to analyze impedance data associated with Cronidur 30 and M50 steel samples in new and degraded jet engine oil. The analysis for the degraded oil included both determining the error structure associated with the data and evaluating the consistency of the data with Kramers–Kronig relations. Voigt measurement model parameters were used to identify characteristic time constants for new and degraded oils. This information was used to differentiate the impedance responses into bulk oil and alloy-oil interfacial contributions. The analysis presented here represents a step toward understanding the physical processes involved.

© 2005 Published by Elsevier Ltd.

Keywords: Impedance spectroscopy; Measurement model; Equivalent circuit; Jet engine oil; M50; Cronidur 30

1. Introduction

Recent advances in propulsion turbo-machinery require development of new high-performance rolling element bearing and lube systems. Current state-of-the-art and advanced bearing materials, such as M50, Pyrowear 675, and Cronidur 30, may be exposed to corrosive environments during the service life of the aerospace applications. This is of particular concern to the bearing, gear and swash plate designs being considered for the new generation aircrafts, as well as current aerospace applications that are exposed to salt water environments.

The environment of concern is a mixture of lubricant, water, and impurities, such as salts, under oxidizing conditions. Jet engine lubricating oils are complex blends of esters designed to remove and dissipate heat. Additives are used to prevent wear and to prevent corrosion and rust. In addition, the oil is designed to be compatible with materials of construction, to resist breakdown from extreme heat and oxygen, to flow freely at very low temperatures, and to maintain performance under adverse conditions. A typical new jet engine oil comprises polyol esters (94–97% by volume), anti-oxidants (2–4%), anti-wear/extreme pressure agents (1–3%), corrosion inhibitors (<0.5%), rust inhibitors (<0.5%) and anti-foam agents (at the ppm level).

The application of electrochemical impedance spectroscopy (EIS) for characterizing metal-lubricant interfacial phenomena has been reported in literature. In these applications, the data were resolved into bulk and interfacial contributions using two RC elements in series. The objective of this work was to explore the use of EIS sensitivity to evaluate phenomena occurring at the metal/oil interface for the steels in oil media using the Voigt measurement model. Voigt measurement models were regressed to the data to determine the characteristic time constants that could be resolved. The regression of the data associated with the degraded oil was used to assess the error structure and to ascertain the degree of stationarity of the data. The characteristic time constants were used to differentiate the impedance responses into bulk oil and alloy-oil interfacial contributions. The analysis presented here represents a step toward understanding the physical processes involved.
The three-probe EIS experiments were conducted using a standard corrosion cell supplied by Princeton Applied Research (model K0047). Samples were mounted in the corrosion cell supplied by Princeton Applied Research. Two samples of the same alloy were mounted in two holders with an exposed surface of 1 cm² for each holder. The holders were placed in the cell. The reference electrode was positioned approximately 1–2 mm from the sample using a Luggin tube.

The two-probe EIS experiments were conducted using a sample holder supplied by Princeton Applied Research. Two samples of the same alloy were mounted in two holders with an exposed surface of 1 cm² for each holder. The holders were placed in a beaker such that the faces of the samples were parallel to each other and separated by 6 mm. The beaker was filled with the oil to a level such that the holders were totally immersed. A thermometer was also placed in the beaker to monitor temperature changes.

The preparation procedure for the samples included polishing to a 600 grit finish, then washing sequentially in acetone, methanol, and deionized water. The samples were left standing in air for approximately 15 h to permit formation of protective oxide layers. The new and degraded oil used in the experiments were supplied by Pratt and Whitney. The degraded oil was prepared following FED STD 791 Method 3308 [7]. New jet engine oil was heated to 400°F until the Acid Number, measured using ASTM D664 [8], reached a value of 1.0 mg KOH g⁻¹. The intent of the degradation procedure was to simulate the working conditions under which the oil would be exposed in the jet engine. The effect of the degradation procedure was the partial de-esterification of the polyol ester that was the primary constituent of the oil.

All experiments were carried out using a PC4 Potentiostat supplied by Gamry Instruments, Inc., and acquisition of data was performed using the Gamry Instruments EIS300 Electrochemical Impedance Spectroscopy System (version 3.20). The experiments were performed in a Faraday cage, to reduce the influence of surrounding electromagnetic fields. The assembled apparatus was placed in a water bath to maintain the temperature of the corrosion cell. A 10 min period was used to allow the sample sufficient time to equilibrate with the surroundings before the first scan was taken. Scans took approximately 20–25 min for the frequency range of 10 kHz to 0.01 Hz. Ten-minute intervals were used between scans to allow the sample to re-equilibrate with the surroundings. The impedance scans were performed against open circuit potential. The temperature at the beginning and end of each scan was recorded.

### 3. Experimental results

Impedance data collected for the Cronidur 30 alloy in the new oil and degraded oil using the three-probe cell are shown in Fig. 1a and b, respectively. The data obtained in the new oil for frequencies greater than 6.31 Hz included large scatter and
Fig. 1. Sequential impedance spectra for Cronidur 30 alloy in jet engine oil obtained using a three-probe EIS experimental setup. (a) New jet engine oil and (b) degraded jet engine oil.

are not reported here. The temperature for the scans shown in Fig. 1a for new oil was 18.3 ± 0.1 °C. The oil temperature during the course of the experiments performed in the degraded oil decreased from 19.5 to 18.8 °C. The impedance data for Cronidur 30 in the degraded oil revealed both capacitive and pseudo-inductive behavior. Through a series of experiments not reported here, it was determined that the majority of the pseudoinductive behavior could be attributed to the use of a glass frit to separate the reference electrode from the oil phase. The results presented in Fig. 1 are included here to demonstrate the inapplicability of an aqueous-based reference electrode such as the saturated calomel electrode for EIS experiments in non-aqueous media and to motivate use of the two-electrode cell design.

Impedance data obtained for M50 and Cronidur 30 using the two-electrode cell are shown in Fig. 2a and b, respectively,

Fig. 2. Sequential impedance spectra for stainless steel in jet engine oil obtained using a two-probe EIS experimental setup. (a) M50 and (b) Cronidur 30 in new jet engine oil. (c) M50 and (d) Cronidur 30 in degraded jet engine oil.
for data collected in the new oil. Corresponding data collected in degraded oil are presented in Fig. 2c and d, respectively. The time of immersion is given as a parameter. There was little temperature variation during the course of the experiments. The temperature for the scans associated with M50 and Cronidur 30 in the new oil was 20.4 ± 1.0°C. The temperatures for the scans associated with M50 and Cronidur 30 in the degraded oil were 21.2 ± 0.1°C and 20.5 ± 0.1°C, respectively. The drift in the impedance scans seen in the figures was attributed to a phenomenon which required greater than 10 min to equilibrate. This drift was more pronounced in the degraded oil as compared to the new oil.

A frequency range of 10 kHz to 0.01 Hz was used for the impedance measurements given in Fig. 2. For the analysis discussed in the following section, impedance data with negative real parts (ranging from 10 kHz to 2.5 kHz) were truncated.

4. Measurement model analysis

The measurement model technique has been used in literature to distinguish between bias and stochastic errors associated with impedance spectra [9–11]. The method uses a generalized Voigt model to filter the replication errors of the Kramers–Kronig relations; thus, the measurement model can be used to determine the internal consistency of data without explicit integration of the Kramers–Kronig relations [11]. The determination of consistency was performed using an overall error analysis that used a weighting strategy based on the measured stochastic error structure.

4.1. Technique

The analysis of impedance data using the measurement model technique is demonstrated using the data associated with the 45, 80, and 115 min immersion times of M50 in degraded oil. The maximum number of Voigt elements that could be resolved for each scan was five. A value of \( R_0 = 0 \) was used in the Voigt measurement model as a nonzero value could not be resolved with satisfactory confidence from the experimental impedance data. The parameters for the Voigt measurement model regressed for M50 data are given in Table 2 in which modulus weighting was used. The parameters included the resistance and time constant associated with each Voigt element. The error associated with a given parameter was calculated using a linear approximation.

The measurement model technique was used to assess the consistency of the impedance data with Kramers–Kronig relations. The procedure used was reported by Agarwal et al. [10] and utilized by Orazem [12] and Shukla et al. [13]. In this procedure, the variances of the real and imaginary residual errors were obtained as a function of frequency. A good estimate of the variance of the stochastic errors can be provided by this function under the following assumptions outlined by Shukla et al. [13]:

\( R_0 \) and \( \tau_0 \) were used in the Voigt measurement model as a nonzero value could not be resolved with satisfactory confidence from the experimental impedance data. The parameters for the Voigt measurement model regressed for M50 data are given in Table 2 in which modulus weighting was used. The parameters included the resistance and time constant associated with each Voigt element. The error associated with a given parameter was calculated using a linear approximation.

4. Measurement model analysis

The measurement model technique has been used in literature to distinguish between bias and stochastic errors associated with impedance spectra [9–11]. The method uses a generalized Voigt model to filter the replication errors of the Kramers–Kronig relations; thus, the measurement model can be used to determine the internal consistency of data without explicit integration of the Kramers–Kronig relations [11]. The determination of consistency was performed using an overall error analysis that used a weighting strategy based on the measured stochastic error structure.

4.1. Technique

The analysis of impedance data using the measurement model technique is demonstrated using the data associated with the 45, 80, and 115 min immersion times of M50 in degraded oil. The maximum number of Voigt elements that could be resolved for each scan was five. A value of \( R_0 = 0 \) was used in the Voigt measurement model as a nonzero value could not be resolved with satisfactory confidence from the experimental impedance data. The parameters for the Voigt measurement model regressed for M50 data are given in Table 2 in which modulus weighting was used. The parameters included the resistance and time constant associated with each Voigt element. The error associated with a given parameter was calculated using a linear approximation.

The measurement model technique was used to assess the consistency of the impedance data with Kramers–Kronig relations. The procedure used was reported by Agarwal et al. [10] and utilized by Orazem [12] and Shukla et al. [13]. In this procedure, the variances of the real and imaginary residual errors were obtained as a function of frequency. A good estimate of the variance of the stochastic errors can be provided by this function under the following assumptions outlined by Shukla et al. [13]:

(1) The model parameters account for systematic differences among imperfectly replicated spectra.

**Table 2** Model parameters for the fit to a Voigt measurement model for the impedance data for M50 stainless steel in degraded oil

<table>
<thead>
<tr>
<th>Parameter</th>
<th>45 min</th>
<th>80 min</th>
<th>115 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_0 ) (MΩ cm²)</td>
<td>0.43 ± 0.07</td>
<td>0.20 ± 0.03</td>
<td>0.21 ± 0.03</td>
</tr>
<tr>
<td>( \tau_0 ) (ms)</td>
<td>0.26 ± 0.03</td>
<td>0.14 ± 0.02</td>
<td>0.12 ± 0.02</td>
</tr>
</tbody>
</table>

**Fig. 3.** A schematic representation of a Voigt circuit used by Agarwal et al. [9–11] as a measurement model.
(2) The frequency-dependent systematic errors associated with the lack of fit are unchanged from one scan to another.

(3) The systematic errors associated with instrument artifacts are unchanged from one scan to another.

(4) The systematic error associated with nonstationary behavior is unchanged from one scan to another.

The standard deviation of the stochastic errors can be identified from the standard deviation of the residual errors under the assumptions given above. The standard deviations of the real and imaginary parts of the impedance data as a function of frequency are shown in Fig. 4. The model for the standard deviation proposed by Orazem et al. [14] was used, where $R_m$ is the current measuring resistor used in the experiment, and $\alpha$, $\beta$, $\gamma$, and $\delta$ are constants to be determined.

$$\sigma_{Z_r} = \sigma_{Z_j} = \alpha |Z_j| + \beta |Z_r| + \gamma |Z_j|^2 + \delta$$

(2)

The value of $R_m$ associated with the impedance measuring system was $10^3 \Omega$.

The consistency of a given data set with respect to Kramers–Kronig relations was determined by first fitting to the imaginary part of the spectrum using the experimentally determined error structure to weight the regression. The maximum number of statistically significant Voigt elements was used in the fit. The parameter set obtained was then used to predict the real part of the spectrum. Monte Carlo simulations were used to obtain the 95.4% confidence interval for the prediction. Comparison of the experimental imaginary part and the predicted confidence interval indicated which data may be inconsistent with the Kramers–Kronig relations.

### 4.2. Assessment of consistency with the Kramers–Kronig relations

The results for the fit of the Voigt measurement model to the imaginary part of the impedance spectrum of M50 (115 min) in degraded oil are presented in Fig. 5a. The real part of the impedance, predicted using the parameters obtained from the regression to the imaginary part, is presented in Fig. 5b. The corresponding residual errors are presented in Fig. 6a, where the dotted lines represent the $\pm 2\sigma$ bound for the stochastic errors. The residual errors were of the same order of magnitude as the noise level.

The relative errors for the prediction of the real part are shown in Fig. 6b. The dashed lines in Fig. 6b represent the 95.4% confidence interval for the model and were obtained by Monte Carlo simulation using the calculated confidence intervals for the estimated parameters. The predicted real part for M50 was consistent with the experimental data except at high frequencies. The data collected at the five highest frequencies were outside the 95.4% confidence interval for the M50 steel. These data were therefore deemed inconsistent with Kramers–Kronig relations and were not included in the regressed data for M50 (115 min). Similar results were found for Cronidur 30 (115 min). The data obtained using new oil were too scattered to permit measurement model analysis of consistency with the Kramers–Kronig relations.
4.3. Results of measurement model regression

The Voigt measurement model was regressed to the data obtained with the alloys in the new oil medium using modulus weighting. Five Voigt elements could be resolved. The regressed parameters obtained after 115 min of immersion are shown in Table 3. The errors associated with the parameters corresponded to ±2σ where the standard deviation for parameter estimates was obtained using a linear approximation. The parameter estimates for Voigt elements are presented in order of increasing time constant τk (note the change in units for the time constant). The characteristic frequencies corresponding to each time constant are also presented.

A similar regression was performed for the impedance response of M50 and Cronidur 30 in degraded oil. The regressions were weighted by the inverse of the variance of the data, obtained by use of the measurement model (see Fig. 4). Five Voigt elements could be resolved for M50, and six could be resolved for Cronidur 30. The regressed parameters obtained after 115 min of immersion are also shown in Table 3. A comparison between the data and the regressed model is presented in Fig. 7b for data obtained in new and degraded oil.

Table 3
Regressed Voigt measurement model parameters for data collected after 115 min of immersion

<table>
<thead>
<tr>
<th>Element</th>
<th>Variable</th>
<th>New oil</th>
<th>Cronidur 30</th>
<th>Degraded oil</th>
<th>Cronidur 30</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1 (MΩ cm²)</td>
<td>0.23 ± 0.06</td>
<td>0.20 ± 0.05</td>
<td>0.47 ± 0.14</td>
<td>0.58 ± 0.20</td>
<td></td>
</tr>
<tr>
<td>t1 (ms)</td>
<td>0.20 ± 0.05</td>
<td>0.19 ± 0.04</td>
<td>0.24 ± 0.09</td>
<td>0.32 ± 0.11</td>
<td></td>
</tr>
<tr>
<td>f1 (Hz)</td>
<td>456</td>
<td>855</td>
<td>655</td>
<td>490</td>
<td></td>
</tr>
<tr>
<td>R2 (MΩ cm²)</td>
<td>4.2 ± 1.2</td>
<td>5.7 ± 1.7</td>
<td>13.3 ± 1.6</td>
<td>33 ± 2</td>
<td></td>
</tr>
<tr>
<td>t2 (ms)</td>
<td>4.1 ± 1.0</td>
<td>5.4 ± 1.3</td>
<td>3.13 ± 0.36</td>
<td>3.2 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>f2 (Hz)</td>
<td>39</td>
<td>30</td>
<td>51</td>
<td>49</td>
<td></td>
</tr>
<tr>
<td>R3 (MΩ cm²)</td>
<td>280 ± 30</td>
<td>410 ± 30</td>
<td>730 ± 100</td>
<td>750 ± 130</td>
<td></td>
</tr>
<tr>
<td>t3 (ms)</td>
<td>63 ± 5</td>
<td>78 ± 4</td>
<td>34 ± 4</td>
<td>30 ± 4</td>
<td></td>
</tr>
<tr>
<td>f3 (Hz)</td>
<td>2.5</td>
<td>2.0</td>
<td>4.7</td>
<td>5.4</td>
<td></td>
</tr>
<tr>
<td>R4 (MΩ cm²)</td>
<td>4,800 ± 1,500</td>
<td>15,100 ± 500</td>
<td>710 ± 100</td>
<td>830 ± 120</td>
<td></td>
</tr>
<tr>
<td>t4 (s)</td>
<td>0.57 ± 0.07</td>
<td>0.76 ± 0.02</td>
<td>7.0 ± 4</td>
<td>64 ± 7</td>
<td></td>
</tr>
<tr>
<td>f4 (Hz)</td>
<td>0.28</td>
<td>0.21</td>
<td>2.3</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>R5 (MΩ cm²)</td>
<td>5,500 ± 1,500</td>
<td>5,100 ± 500</td>
<td>0.017 ± 0.004</td>
<td>0.060 ± 0.014</td>
<td></td>
</tr>
<tr>
<td>t5 (s)</td>
<td>1.2 ± 0.1</td>
<td>2.5 ± 0.2</td>
<td>7.5 ± 3.2</td>
<td>0.4 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>f5 (Hz)</td>
<td>0.13</td>
<td>0.063</td>
<td>0.02</td>
<td>0.39</td>
<td></td>
</tr>
<tr>
<td>R6 (MΩ cm²)</td>
<td>–</td>
<td>–</td>
<td>0.022 ± 0.004</td>
<td></td>
<td></td>
</tr>
<tr>
<td>t6 (s)</td>
<td>–</td>
<td>–</td>
<td>6.2 ± 2.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>f6 (Hz)</td>
<td>–</td>
<td>–</td>
<td>0.03</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The results in new oil were obtained using modulus weighting, whereas, the results in degraded oil were obtained using the experimentally determined error structure. Note the change in units for the time constant.
5. Discussion

The alloy-oil systems investigated using the two-electrode system could be distinguished by use of electrochemical impedance spectroscopy. The major difference between the impedance response in new oil and degraded oil was that the low frequency asymptote for the real impedance of the new oil was one order of magnitude greater than the low frequency real impedance of the degraded oil. Experiments performed using a gold electrode showed a similar response, suggesting that the large capacitive loop can be attributed to the dielectric response of the oil.

In the absence of a phenomenological model, the analysis of the EIS responses of the alloys in the new and degraded oils was performed using the Voigt measurement model. The Voigt measurement model has been used in literature to deconvolute spectra in terms of the characteristic time constants [15]. The deconvolution is presented as a plot of Voigt element parameters $R_k$ and $\tau_k$ as a function of $\tau_k$. Such plots are presented in Fig. 8a and b using regressed parameter values found for new oil and degraded oil, respectively. The error bars displayed represent $\pm 2\sigma$ using the estimated confidence interval for parameters $R_k$ and $\tau_k$.

Wang and Lee have suggested that the characteristic frequencies associated with the bulk dielectric response of oil are greater than 10 Hz, corresponding to time constants $\tau < 0.016 s$ [3]. Following Wang and Lee, time constants greater than 0.016 s may therefore be associated with phenomena at the metal-oil interface. These phenomena may include a Faradaic charge transfer or other reactions associated with adsorbed species at the alloy-oil interface.

As seen in Table 3, each of the systems investigated revealed two Voigt elements with time constants less than 0.016 s. The error bars associated with these elements for M50 and Cronidur 30 overlap in both Fig. 8a for new oil and Fig. 8b for degraded oil. The overlap of the error bars for M50 and Cronidur 30 at time constants less than 0.016 s suggests that the phenomena are associated with these elements was not influenced by the metal composition. This result is consistent with the suggestion of Wang and Lee that high
Fig. 9. Distribution of Debye relaxation time constants for the Voigt element parameters listed in Table 3. The error bars correspond to ±2σ and were calculated using a linear approximation. (a) M50 and (b) Cronidur 30.

frequency phenomena are associated with bulk properties of the oil and not with surface phenomena.

The representation of time constants in Fig. 8 with metal composition as a parameter was used to show that the high frequency parameters did not depend on which metal was used in the experiment. To see the influence of oil properties, a similar presentation of the data is provided in Fig. 9a and b, respectively, with oil condition as a parameter. The error bars for the two Voigt elements with time constants less than 0.016 s do not overlap. The result that the high-frequency impedance response was insensitive to the metal composition but sensitive to oil condition provides further support for the contention that these features could be attributed to the bulk oil properties.

As seen in Figs. 8 and 9, the Voigt model parameters with time constants greater than 0.016 s were somewhat sensitive to the metal composition, but were more sensitive to the oil condition. The sensitivity to metal composition and oil condition is consistent with the suggestion that the low-frequency impedance response is associated with phenomena at the metal-oil interface.

6. Conclusions

Electrochemical impedance spectroscopy was shown to be a sensitive tool for differentiating the condition of ester-based jet engine lubricating oils. The impedance response using alloys M50 and Cronidur 30 were less sensitive to metal composition, but differences in low-frequency features were seen. The measurement model technique, used to assess the error structure and to check for consistency with the Kramers-Kronig relations, proved to be useful for differentiating bulk and interfacial contributions to the impedance response.

Acknowledgements

Financial support from Pratt and Whitney is gratefully acknowledged.

References