Mechanism of Ignition of Jet A by Silver Oxide Deposits

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Abstract

Silver oxide deposits with low electrical resistance were formed on a ceramic substrate by bridging two silver conductors of different voltage potential with water. Subsequent, iterative application of voltage to deposits wetted with Jet A eventually resulted in mature deposits capable of dissipating significant electrical energy in the form of heat. The mature deposits, which are composed of primarily carbon and silver, are capable of igniting Jet-A fuel vapor in the vapor space above a heated pool of fuel. Logistics regression analysis indicates that electrical power dissipation in the deposit is a good predictor of ignition. A thermal model and experimental temperature measurements indicate that the deposit can reach temperatures in excess of the hot surface ignition temperature of Jet A.

Introduction



Figure 1. Data acquisition system.

Figure 2. Ignition test fixture schematic.

The voltage was measured directly and the current was determined by measuring the voltage across a precision resistor placed between the dc power supply and the deposit. The voltage during a test was controlled and the current was unconstrained up to the power supply maximum of 6 amps. Ignition testing was performed using a Tag open cup flash-point tester as shown in Figure 2. By holding the Jet A liquid at a constant temperature, a constant fuel-air ratio was produced above the liquid surface. The procedure was similar to an ASTM D1310 flash-point test except the small flame used to test for ignition was replaced with a ceramic insulator on which the silver oxide deposit had been grown. The water bath temperature was maintained at 65.5 °C (150 °F) such that the fuel temperature was nominally 60 °C (140 °F); well above the measured flash point of the commercial Jet A used of 55 °C (131 °F). A temperature controller maintained the temperature of the water bath by controlling the electrical heater of the flash-point tester.



Two ceramic insulator geometries were used to grow the deposit as shown in Figure 3. The flat ceramic insulator shown in Figure 3a was used to grow deposits for material testing and imaging. The cylindrical ceramic insulator shown in Figure 3b was used to record surface temperature and to test for ignition. The cylindrical insulator consisted of a ceramic rod with four 1mm diameter holes parallel to the axis of the insulator. The holes were used to position silver wires and the thermocouple. In each configuration, the separation of the silver conductors was nominally 1 mm.

a) b) Figure 3. Top view of ceramic insulator configurations used to grow and test deposits.

	Table 1. Typical deposit growth sequence								
	Liquid	Liquid	Max. dc	Max.	Max.	Pre-	Post-		
Step	Туре	Vol. (µL)	Volts (V)	Current (A)	Power (W)	Resistance (Ω)	Resistance (Ω)		
1	Water	10	12	0.20	2.3	×	260		
2	Water	10	12	0.37	4.4	260	40		
3	Jet A	5	35	0.30	4.1	40	4,200		
4	Water	5	10	0.35	3.5	4,200	4		
5	Jet A	5	35	2.7	20	4	3,600		
6	Water	5	8	0.60	7.7	3,600	4		
7	Jet A	5	35	2.4	13	4	22,000		
8	Water	5	10	0.59	4.5	22,000	35		
9	Jet A	5	12	4.2	21	35	29		
10	Jet A	5	15	3.8	21	29	57		

Deposit Growth and Evolution

When two silver conductors of different electrical potential are bridged with a drop of deionized water, electrochemistry within the water takes place and oxygen from the water molecules attack the silver to form silver oxide. This silver oxide then settles between the two silver conductors onto the ceramic insulator to form a bridge of silver oxide. A typical deposit growth and evolution sequence is shown in Table 1. First, several water (drop) addition steps are performed until silver oxide bridges the conductors and reduces the resistance to less than 100 ohms. A photographic image of silver oxide filaments formed early in the deposit growth process is shown in Figure 4. A silver oxide deposit with a resistance of less than 100 ohms is shown in Figure 5. Next, Jet A is applied to the deposit and voltage is applied. Initially, this fuel addition step increases the resistance of the deposit. Low resistance is restored by silver oxide deposition with water addition steps. Eventually (Step 9), the resistance is nominally unchanged by the addition of Jet A. This condition is usually synonymous with a deposit that is capable of dissipating significant power, as was the case in Step 9. The images in Figures 6-9 illustrate the process in which the deposit heats up due to power dissipation. At a power level of 5 watts shown in Figure 6, the power dissipation causes smoking. As the power is increased to 8 watts in Figure 7, the deposit begins to turn a faint red color. Increased power of 10 watts, shown in Figure 8, causes the deposit to become noticeably red while power of 13 watts in Figure 9 cause the deposit to become bright red. These images were all taken during the same test as the voltage was increased at a constant rate. The time of the photographs was recorded in the data file such that after the test, the instantaneous values of voltage, current and power could be determined. The elapsed time between the first image (Figure 6) and the last image (Figure 9) is 6 seconds.



Figure 4. Growth of silver oxide filaments bridging electrode gap at low power.



Figure 5. Mature silver oxide deposit, $R < 100\Omega$.



Figure 6. Jet A addition step, Power = 5 W.



Figure 8. Jet A addition step, Power = 10 W.



Figure 7. Jet A addition step, Power = 8 W.



Figure 9. Jet A addition step, Power = 13 W.

Deposit Chemical Composition

Chemical analysis of the deposit by X-ray Photoelectron Spectroscopy (XPS) before the addition of Jet A, after Step 2 in Table 1, confirmed that the deposit was silver oxide. Although the analysis is complicated by common carbon contamination from the atmosphere, it appears that most of the silver oxide present is in the first oxidation state, Ag_2O , but the presence of some AgO is possible. Figure 10 is a scanning electron microscope (SEM) image of a mature deposit that is capable of high power dissipation. Auger Spectroscopy indicated that the surface of the deposit is primarily carbon with less than 10% oxygen and trace amounts of silver. Figure 11 is a close up of one of the spherical features on the surface of the deposit shown in Figure 10. The outer shell was intentionally pulled away from the sphere to facilitate analysis of the material beneath the surface. Auger analysis was performed on the three areas highlighted by white boxes. The results of these analyses are presented below in Table 2.



Figure 10. SEM image of mature deposit.

Figure 11. Close-up of sphere on surface of deposit.

Table 2. Results of Auger analysis for highlighted areas shown in Figure 11.								
Area	Description	% Silver	% Carbon	% Oxygen				
1	Sphere	91.8		8.2				
2	Outside of shell	0.6	97.2	2.1				

3 Inside of shell	12.8	85.5	1.8
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As shown in Table 2, the mature deposit is primarily carbon with silver spheres dispersed on the surface. A cross section of the deposit, shown in Figure 13, confirms the presence of the silver spheres throughout the deposit. The cross section also reveals a layered structure between silver spheres consistent with repeated ignition attempts.

Figure 13. Cross section of mature deposit.

Auger Spectroscopy cannot detect elements with molecular weight less than 5 (boron) and thus cannot be used to determine whether the carbon-based material is a hydrocarbon. Hence, the carbon-based layers were also analyzed using Raman and FTIR Spectroscopy. It was determined that the gray and black carbon-based layers are primarily disordered and graphitic carbon indicating that it was formed at relatively high temperatures. No hydrocarbons were detected.

Reduction of Silver Oxide by Jet A

The reaction of silver oxide with hydrocarbon fuels to produce elemental silver is spontaneous, based on the Gibbs free energy change of the reaction, but is kinetically limited in the case of Ag_2O and Jet A at room temperature. Increasing the temperature of the silver oxide and Jet A mixture, however, will result in a reaction. The temperature at which this reaction occurs was measured to be 136 °C for AgO / Jet A mixture and 164 °C for an Ag_2O / Jet A mixture. Auger analysis of the products revealed that the product was primarily silver (average of 95%) with small amounts of oxygen (average of 5%) and no measurable amounts of carbon.

The ability of Jet A to reduce silver oxide to elemental silver is a crucial factor in the ignition process. Since the deposit is electrically connecting two conductors, current passing through the deposit can result in a temperature rise, especially at a neck in the conductive path where the current density is highest. If the temperature at these locations exceeds the temperature threshold for reaction, silver will be formed. In addition, partial oxidation of the fuel appears to form carbon in the deposit. These reactions would likely disrupt the structure of the deposit, which is consistent with the resistance increase after the initial Jet A addition steps shown in Table 1. Subsequent water addition steps can redeposit silver oxide in gaps in the newly formed silver and carbon or form new filaments that lower the resistance. Repeated applications of Jet A will continue the conversion process until a mature deposit consisting of mostly carbon and silver is formed. This mature deposit is capable of withstanding and dissipating relatively high power; and, consequently, can generate enough heat and high temperatures to ignite nearby flammable fuel vapors.

Thermal Model

A thermal model of the ceramic insulator illustrates that measured electrical power dissipation within the deposit can produce surface temperatures sufficient for hot surface ignition. The model assumes convection losses on the sides, a uniform heat flux on the top surface and uniform temperature in the r-direction as shown in Figure 14. Based on the time duration of measured electrical power, the penetration depth is less than the length of the ceramic insulator. Therefore, the boundary condition at the bottom surface has minimal impact on the solution and is

assumed to be adiabatic for simplicity. The governing partial differential equation and boundary conditions are as shown below:



Figure 14. Schematic of thermal model boundary conditions.

$$\frac{\partial T}{\partial t} - \alpha \frac{\partial^2 T}{\partial x^2} + \frac{hP}{\rho cA} \left(T - T_{\infty} \right) = 0 \tag{1}$$

$$\left. \frac{\partial T}{\partial x} \right|_{x=0} = -\frac{q_i}{k} \tag{2}$$

$$\left. \frac{\partial T}{\partial x} \right|_{x=l} = 0 \tag{3}$$

$$T(0,z) = T_i(x) \tag{4}$$

Although the problem statement above requires that the power dissipation on the top surface be constant, a variable power problem can be solved by dividing the problem into numerous segments and solving each segment with the average power in the segment. The initial condition (4) is then the temperature solution from the previous segment. The solution to the above problem is given by

$$T(t,x) = \frac{q}{km} \frac{\cosh(ml)}{\sinh(ml)} \cosh(mx) - \frac{q}{km} \sinh(mx) + T_{\infty} + \sum_{n=0}^{\infty} C_n e^{-(m^2 + \lambda_n^2)\alpha t} \cos(\lambda_n t)$$
(5)

where

$$C_{0} = \frac{-q_{i}}{km^{2}l} + \frac{1}{l} \int_{0}^{l} T_{i}(x) dx \quad n = 0 \qquad \qquad m = \sqrt{\frac{hP}{kA}}$$
$$C_{n}' = \frac{-2q_{i}}{kl(m^{2} + \lambda_{n}^{2})} + \frac{2}{l} \int_{0}^{l} T_{i}(x) \cos(\lambda_{n}x) dx \quad n = 1, 2, 3, ... \qquad \qquad \lambda_{n} = \frac{n\pi}{l}$$

When the duration of the power dissipation was relatively long, the computed temperature in Eq. (5) showed general agreement with the measured temperature as shown in Figure 15. As shown in Figure 3, the thermocouple for this measurement was located about 1 mm from the centerline of the deposit and the data was not corrected for any r-direction temperature gradients. The measured surface temperature exceeds the known hot surface ignition temperature of Jet A of 538 °C to 641 °C (Myronuk 1980) and even approaches the melting point of silver of 962 °C (Lide 1995). The melting of the silver deposit may explain why the model predicts a higher temperature. In tests when the time of the heat dissipation is short (< 10 seconds), the model greatly under predicts the temperature data. This discrepancy is likely due to significant temperature variation in the r-direction of the ceramic insulator

which is not accounted for in the model. A logistic regression between maximum test power and ignition for a set of 221 ignition tests shows that maximum power is a good predictor of ignition as evident in Figure 16.



Figure 15. Measured and computed surface temperatures for a test that caused ignition. Maximum test power was 27 watts.

Figure 16. Logistic regression of ignition probability versus maximum test power. Solid circles = ignition, open circles = no ignition

Conclusions

Silver oxide deposits can be formed electrochemically when water bridges two silver conductors with different voltage potential. The silver oxide and Jet A can be reduced to silver and carbon if the temperatures resulting from localized current density are sufficiently high. Deposits containing a large portion of carbon and silver are capable of high power dissipation that can produce surface temperatures exceeding the hot surface ignition temperature of Jet A. A thermal model of the power dissipation process indicates that electrical power alone is sufficient to cause hot surface ignition. Logistic regression on a series of ignition tests shows that ignition probability is strongly correlated with electrical power dissipation.

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