

Hot Surface Ignition by Oxidized Nickel Surfaces

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1 Introduction

The effect of surface-oxide scales on gas-phase ignition of flammable hydrogen-air mixtures by hot metallic surfaces was investigated experimentally. The surface temperature required to induce combustion in an adjacent flammable mixture is typically referred to as the hot surface ignition temperature (HSIT). Hot surface ignition temperatures have been found to depend on many factors including the flammable mixture properties, the flow field near the hot surface, surface geometry and orientation, and the material and condition of the hot surface [1]. While metal surfaces that oxidize at high temperature are often included in experimental hot surface ignition studies, no systematic investigations focusing on the effect of surface preparation and surface-oxide structure have been conducted.

2 Experimental Setup and Procedure

Ignition experiments were performed in a continuous-flow axisymmetric finite-gap stagnation-flow reactor using ultra-high purity premixed hydrogen-air mixtures at atmospheric pressure. The experimental apparatus consists of four subsystems: (1) the ignition reactor vessel, (2) the surface heating system, (3) the fuel preparation system, and (4) the control and data acquisition system. A schematic of the complete experimental setup and a diagram of the reactor cross section is shown in Figure 1.

The reactor is a continuous-flow vertical-cylindrical vessel with the gas inlet at the bottom and the discharge at the top. The heated stagnation surface is inserted midway into the chamber volume along the centerline at the discharge end and supported from above by an adjustable rail on the test stand. Gas flow through the vessel is directed vertically upward at a constant inlet gas velocity of 0.66 cm s^{-1} so that the buoyant forces caused by local heating of the gas mixture near the stagnation surface do not compete with the forced gas flow causing instabilities and/or recirculation zones. Premixed gas is introduced at the bottom of the reactor along the centerline. The gas flows through a flow distribution and straightening section and a bed of 3-mm diameter borosilicate glass beads 45 mm deep. A floating, porous annular-shaped free-floating aluminum plate is used to cover the reactor outlet.

The heater/surface system consists of a separate coupon of surface material that is mechanically attached to the surface heater. The heater is a custom built electric resistance heater. The stagnation surface is a 25.4-mm diameter metal disk 2.8 mm thick. The surface temperature, T_s , is measured with a 0.5-mm diameter sheathed thermocouple inserted into a hole drilled in the back of the coupon and terminating 0.25 mm below the surface. Stagnation surfaces are made of high-purity gold (99.999%), and nickel (99.99%). Surfaces were polished to a near-mirror finish prior to each ignition experiment.

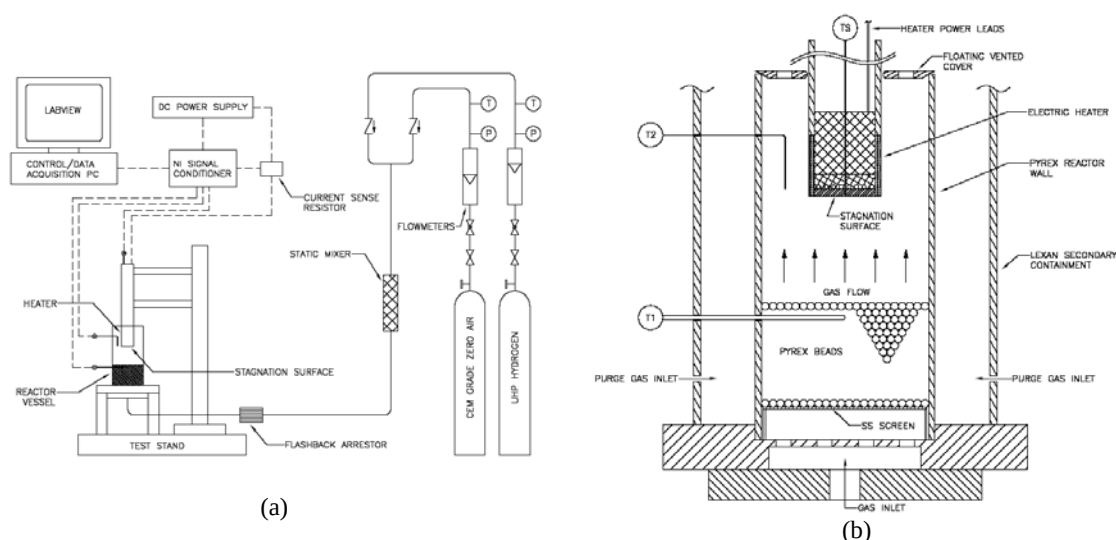


Figure 1. Schematic of complete experimental setup used for hot surface ignition experiments (a), and cross section of ignition reactor vessel (b).

A data acquisition (DAQ) system with National Instruments[®] hardware and Labview[®] software was used to control the Agilent[®] 6543A programmable dc power supply and display and store experimental data. Heater voltage, current and all temperature data were recorded at a sampling rate of 2 Hz.

The primary intent of the ignition experiments was to determine whether the surface oxide has an effect on hot surface ignition temperatures. Instead of pre-oxidizing surfaces to a known condition and then attempting to perform ignition tests in a way that minimizes further changes to the surface, it was decided to begin an ignition test sequence with a polished surface and perform a series of repeated ignition tests using the same coupon to determine whether the hot surface ignition temperature changes as the surface oxidizes. Starting with a polished surface, the reactor was purged with pure hydrogen for about 30 minutes. While maintaining the hydrogen flow rate, the heater power was increased linearly. When the surface temperature reached about 500 – 600 °C, the hydrogen flow rate was reduced from the purge rate to the required set point. Air was introduced into the system when the surface temperature reached 675 °C. The elapsed time for the experiment is measured relative to the point when the air is turned on since the surface begins to oxidize at this point. When ignition occurred, the heater power was immediately reduced to a level that results in a surface temperature approximately 25 to 50 °C below the observed hot surface ignition temperature. The hydrogen and air continue to flow through the reactor vessel. However, a flame is not stabilized on the surface of the bed of glass beads because the hydrogen-air flame speed is approximately 400 times greater than the velocity of the fuel-air mixture in the reactor. As a result, the flame consumes all available reactants and extinguishes at the surface of the bed of glass beads.

After ignition, the heater power was held at the reduced level for 5 minutes, allowing the products of combustion to be purged from the reactor by the incoming reactants. After the purge cycle, the heater power was increased at a constant rate from the reduced level until ignition occurred again. The entire cycle was repeated until the hot surface ignition temperature remained approximately constant for a minimum of 5 consecutive ignition events. Most experiments were performed over a period of 2 to 3 hours, or 15 to 20 ignition events.

3 Results

A summary of ignition test results is presented in Figure 2. Because the gold surface does not oxidize in the presence of oxygen at high temperature, gold serves as a good reference material to validate the repeatability of

the experiment and to provide a baseline to which materials that oxidize can be compared. For the 5 sets of experiments shown in Figure 2, the standard deviation for 5 repeats at each equivalence ratio ranges from 0.29 to 0.95 °C. The corresponding half-width of the 95% confidence intervals shown in Figure 2 ranges from 0.36 to 1.32 °C. These small error bands verify that the experimental setup and procedure generate repeatable results with relatively little noise for a surface that does not change during the testing process. The HSIT with the gold surface increased monotonically with equivalence ratio from 714 to 724°C. Enomoto *et al.* [2] measured comparable values with a similar experimental approach.

In contrast to the results for gold surfaces, the ignition temperature for nickel surfaces at certain equivalence ratios changes during the course of the experiment as the surface oxidizes. As a result, Figure 2 includes two curves for ignition experiments with nickel surfaces; one for polished surfaces and one for 'mature' surfaces. The data for polished surfaces is the average of the first two ignition events in a series starting with an initially polished surface. The data for mature surfaces is the average of the last two of 15 ignition events in a series. The HSIT increased monotonically with equivalence ratio for both polished and oxidized surfaces. At all equivalence ratios investigated, the nickel surface oxidized during the ignition test sequence. As is evident from Figure 2, the presence of the oxide does not affect the HSIT at an equivalence ratio of 0.3. At higher equivalence ratios the HSIT increased during the test sequence with higher equivalence ratios producing greater increases. At an equivalence ratio of 0.3 the HSIT on nickel is 728°C. At an equivalence ratio of 1.0, the HSIT on nickel surfaces is 768°C and 844°C for nearly-polished and mature surfaces, respectively.

Several additional experiments were performed at an equivalence ratio of 0.5 with nickel surfaces to determine whether the presence of the oxide alone inhibits ignition or whether the oxide structure changes in a way that inhibits ignition. The ignition experiments were performed with nickel surfaces that were pre-oxidized at 700°C for 2 hours in air and in a hydrogen-air mixture at an equivalence ratio of 0.5. The air oxidized surface produced ignition results similar to those of an initially polished surface; the ignition temperature was initially low and increased over the course of 15 consecutive ignition events. The surface that was oxidized in the hydrogen-air mixture produced ignition results similar to the mature nickel oxide surfaces; they produce high ignition temperatures similar to those observed at the end of an ignition test sequence. The HSIT produced by the surface oxidized in the hydrogen-air mixture did not change during the ignition test sequence. These results indicate that the HSIT over oxidized nickel surfaces is inhibited not by the presence of an oxide (formed in air) alone but by changes in the structure that result from exposure to the hydrogen-air mixture at high temperatures.

The nickel oxide surfaces were characterized with scanning electron microscopy and focused ion beam microscopy to determine whether any measurable changes in surface properties correlate with the observed changes in ignition temperatures. In general, lower equivalence ratios produced thicker oxide layers that were not porous. Higher equivalence ratios produced porous oxide layers. Figure 3 shows two SEM micrographs of nickel oxide layers formed at 700°C for 2 hours in air and in a hydrogen-air mixture. The oxide formed in air is not porous and is 2.0 µm thick. The oxide formed in hydrogen-air is porous across the entire thickness and is only 1.1 µm thick. Ignition experiments that are performed with initially polished nickel surfaces produce porous oxide layers that are nearly identical to those formed by preoxidizing in hydrogen-air. After a subsequent ignition test sequence, the non porous oxide that was formed by preoxidizing in air is converted to a porous oxide layer.

5 Conclusions

Hot surface ignition temperatures with gold surfaces increased monotonically with equivalence ratio from 714 to 724 °C and were independent of surface condition. Hot surface ignition temperatures with nickel surfaces increased monotonically from 728 to 843 °C and demonstrated a strong dependence on surface condition.

Surface characterization with scanning electron microscopy and focused ion beam microscopy confirmed that changes in the micro-structure of the metal-oxide scales could alter the observed hot surface ignition temperatures by up to 75 °C.

Care should be exercised when interpreting hot surface ignition data for surface materials that oxidize under conditions that are capable of supporting gas phase combustion.

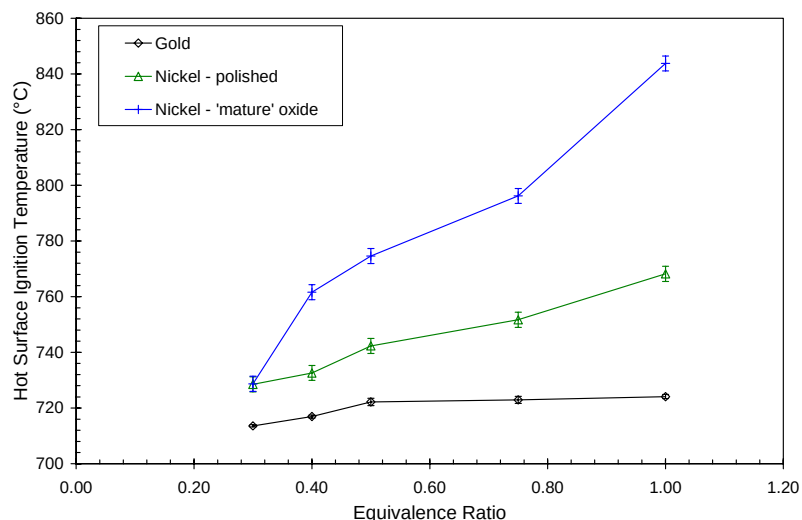


Figure 2. Summary of hot surface ignition temperatures versus equivalence ratio for gold and nickel.

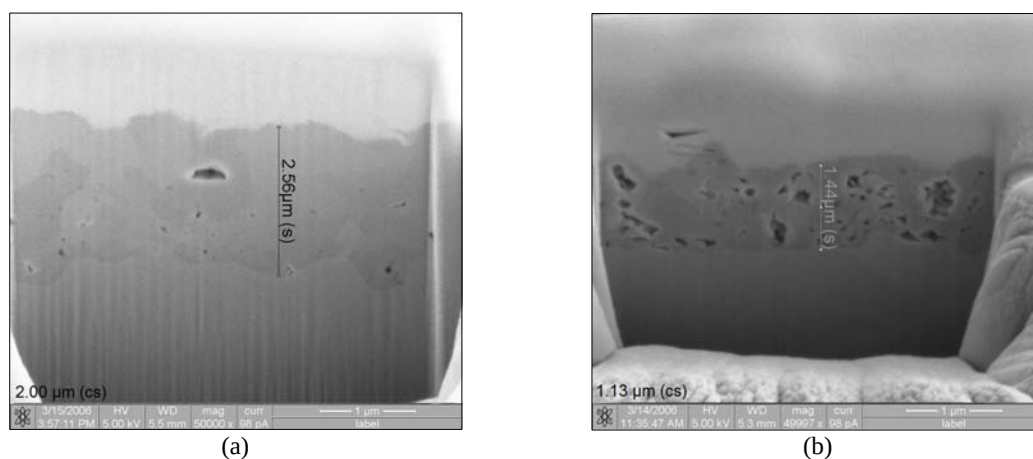


Figure 3. SEM micrographs of nickel oxide cross-section formed by oxidizing a polished nickel coupon for 2 hr at 700 °C in air (a), and at an equivalence ratio of 0.5 (b).

References

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- [2] Enomoto, K, Furuhashi, S and Kobayashi, Y (1981). Ignitability of hydrogen-air mixture by hot surfaces and hot gases. Hydrogen Energy Progress, 2: 1149