

Determination of Oxidation Characteristics and Studies on the Feasibility of Metallic Nanoparticles Combustion Under ICE-Like Conditions

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ABSTRACT

The present work relates to the investigation of the basic oxidation characteristics of iron and aluminium nanoparticles as well as the feasibility of their combustion under both Internal Combustion Engine (ICE)-like and real engine conditions. Based on a series of proof-of-concept experiments, combustion was found to be feasible taking place in a controllable way and bearing similarities to the respective case of conventional fuels. These studies were complimented by relevant in-situ and ex-situ/post-analysis, in order to elaborate the fundamental phenomena occurring during combustion as well as the extent and 'quality' of the process. The oxidation mechanisms of the two metallic fuels appear different and -as expected- the energy release during combustion of aluminium is significantly higher than that released in the case of iron. The peak gas temperatures recorded during combustion of iron under engine-like and real engine conditions indicate that the NO_x formation threshold is not reached. Combustion of aluminium yields substantially higher peak combustion temperatures and thus it is likely that is accompanied by NO_x emissions. In addition, the experimental results provided indication that the approach of Exhaust Gas Recirculation (EGR) could be an efficient means of controlling the combustion process.

INTRODUCTION

The possibility of utilising metals as potential energy carriers and/or fuels for Internal Combustion Engines (ICE) has first been considered a few decades ago. The idea lies on two main characteristics: some metals contain significantly higher energy content per unit volume than the conventional liquid fuels, while -under certain conditions- the only product derived from their combustion is the respective metal oxide. In principle, the latter makes metals excellent candidate fuels towards the implementation of the so-called zero-emission combustion engines, since all pollutants derived from the combustion process of the conventional liquid fuels are avoided. The environmental friendliness of the concept can be further strengthened under the prerequisite that the metal oxide (spent fuel) is recycled so that the metal is recovered and reused. In the case of iron and aluminium, which are two relatively abundant and non-toxic metals, their oxidation reactions can be written as follows:

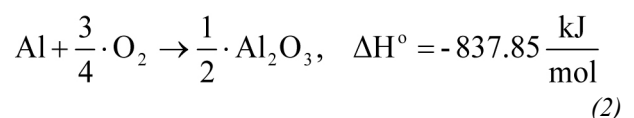
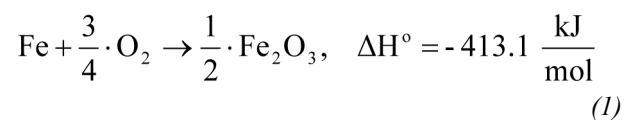


Table 1. Main physicochemical characteristics of utilised metallic nanopowders.

Nanopowder	Estimated Average Primary Particle Size (nm)	Average thickness of oxide layer (nm)	BET (m ² /gr)	Phases identified by XRD	Maximum (theoretical) weight increase due to oxidation
Fe50	50	2-3	9.3	metallic Fe	38%
Fe85	85	2	12.7	metallic Fe	39.5%
Al50	50	2-3	32.8	metallic Al	71%

The fundamental problem, when considering such metals in the form of chunks or micron-sized powders, is the fact that their ignition is difficult. However, upon ignition the combustion process proceeds in an uncontrollable way, thus resulting to extremely high temperatures and making the whole process unsuitable for ICE applications. This is the main reason why, until very recently, virtually all existing studies and practical applications of metal-based fuels refer to rocket propellant related applications [1,2,3,4]. The most suitable way of achieving good control of a metallic fuel combustion process is by tuning the size of its primary particles. Indeed, the recent advances of nanotechnology in the manufacturing of metallic nano-powders with specific tailored characteristics have opened new pathways in the exploitation of such novel energy carriers. In particular, very preliminary studies indicated that in the nanoscale regime metallic powders, such as iron and aluminium, are combustible in timescales comparable with the ones of engine cycle and the phenomenon occurs either in solid or liquid state [5, 6]. The increased reactivity and controllability of nanopowders oxidation process, within reasonable ranges of temperature and pressure conditions, is attributed to their substantially high surface area [2].

EXPERIMENTAL

The metal fuels investigated in the current work included two different iron nanopowders (one prepared by reduction of Fe₂O₃ nanopowder with H₂ and one commercially available) and an aluminium one. All nanopowders were subjected to fundamental Thermo Gravimetric Analysis (TGA) under varying oxygen content, as well as to proof-of-concept studies in order to exploit their fundamental engine-like and real engine combustion characteristics. The engine-like tests refer to shock-tube and constant-volume high-temperature vessel (combustion bomb) experiments. The combustion process in these tests was explored by means of optical diagnostic techniques. Both (Fe and Al) metal fuels were utilised and their respective combustion products were ex-situ analysed by Transmission Electron Microscopy (TEM)/Energy Dispersive X-ray analysis (EDS) and X-Ray Diffraction (XRD). For the real engine tests, a single cylinder compression-ignition engine was employed.

The aluminium and one of the iron nanopowders (referred to as Al50 and Fe50 respectively) employed in the present studies were obtained from READE Advanced Materials and their purity was 99.9+%. The second iron nanopowder (referred to as Fe85) was produced via reduction with H₂ of an in-house prepared Fe₂O₃ nanopowder. The reduction process was followed by passivation of the resulted Fe nanoparticles (i.e formation of a thin oxide shell around the particles) to avoid undesirable spontaneous ignition phenomena. Displayed in [Table 1](#) are characteristic size parameters of the nanopowders examined along with the analytical techniques used to determine each of these parameters. Representative TEM images are depicted in [Figure 1](#). The commercial nanopowders consisted of almost spherical-shaped primary particles while the in-house iron nanoparticles were irregularly-shaped and highly agglomerated.

The TGA studies were conducted in a Perkin Elmer Pyris-6 instrument under O₂/N₂ mixtures with the O₂ content ranging between 0% and 100%. The gaseous stream was continuously flowing over the tank containing the nanopowder, while temperature was increased from ambient up to 1273 K at a rate of 5 K/min. Structural characterisation of the powders was performed by XRD using a Siemens D-500 Kristalloflex X-ray powder diffractometer (Cu K α radiation). Specific surface area (BET method) was measured with the aid of a nitrogen adsorption porosimeter (Micromeritics ASAP 2000).

Depicted in [Figure 2](#) is the diaphragm type shock-tube system employed. Its running section was 50 mm in internal diameter and 6m long. The measurement section, placed at 20 mm from the end wall, was equipped with optical access areas. The metallic nanopowders were pneumatically injected into the measurement section just prior to shock initiation. The oxidation process was followed by means of optical diagnostics. Extinction measurements in the visible spectrum allowed monitoring of the injection phase as well as the evaluation of particle loading in the measurement section. The temperature of reacting particles was measured by means of two-colour pyrometry.

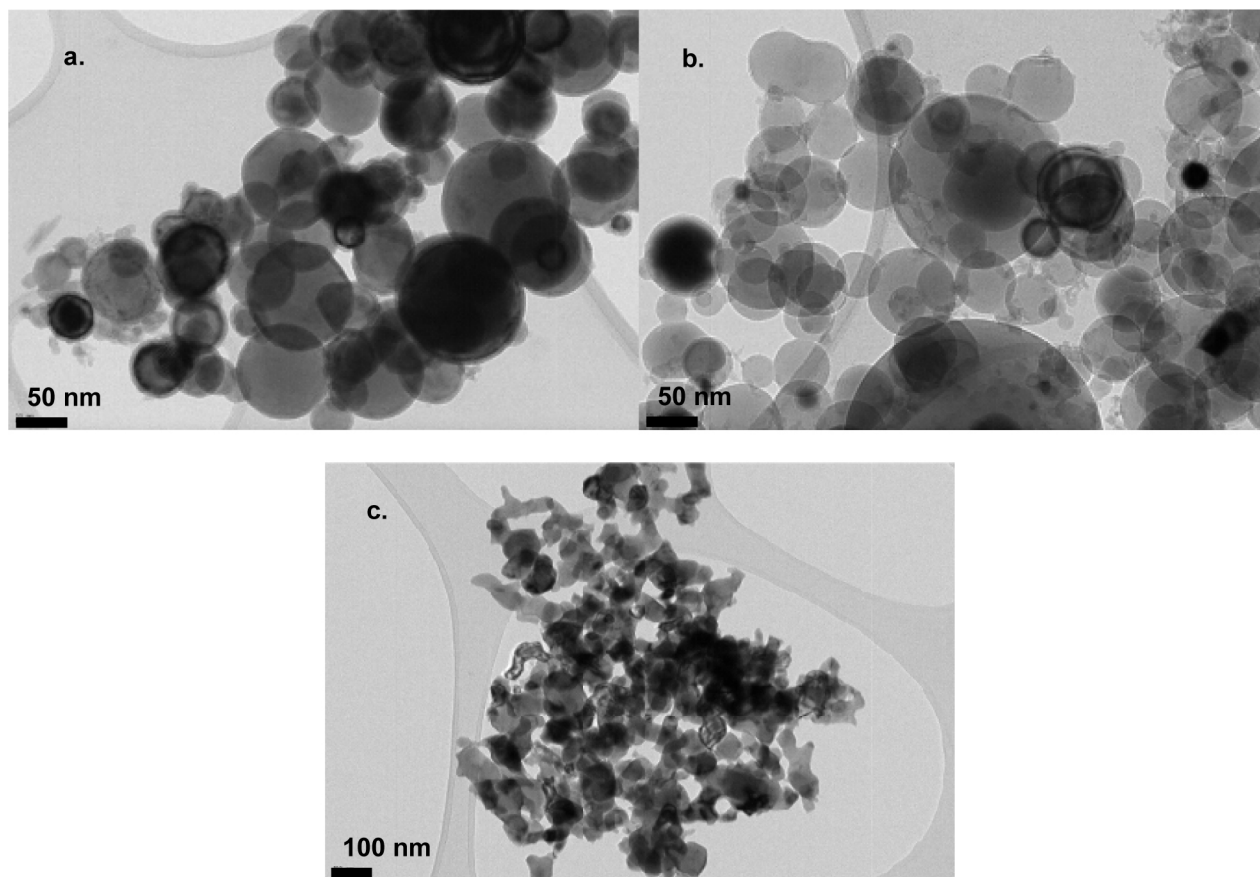


Figure 1. Indicative TEM images of the nanopowders utilised: a. Fe50, b. Al50, c. Fe85.

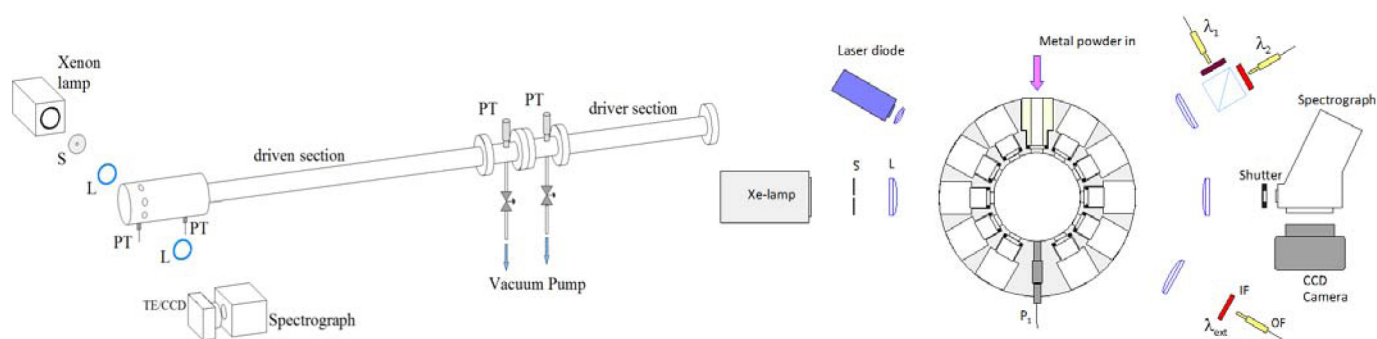


Figure 2. Shock tube layout (left) and its measurement section and optical diagnostics setup (right).

The custom-made constant volume, high-pressure, high-temperature combustion chamber system is illustrated in Figure 3. The vessel was originally designed to reproduce thermodynamic conditions representative of those existing in the cylinder of a real ICE. In addition, it was equipped with adequate optical access thus permitting visualization of the injection/combustion process. Pressure, temperature and O₂ concentration inside the vessel were fully adjustable, hence enabling investigation of the combustion fundamentals under controllable environment. During the experimental process, the vessel was filled with synthetic air up to a target density

and then the air was heated up with a MHI GA-XP coil heater until the target temperature was achieved. The heater was then switched off and few seconds later the metallic fuel was injected. This was done in order to allow for homogenisation of the gas temperature inside the vessel. To reduce heat losses through the walls, a refractory mortar (Greenlite 45 L) was selected for insulation. A pneumatic, powder injection system was designed with the aid of CFD analysis. In this system, nanoparticles were dragged by a gas stream capable of performing isolated injection shots of pre-defined quantities at the desired injection pressure. A shadowgraph arrangement

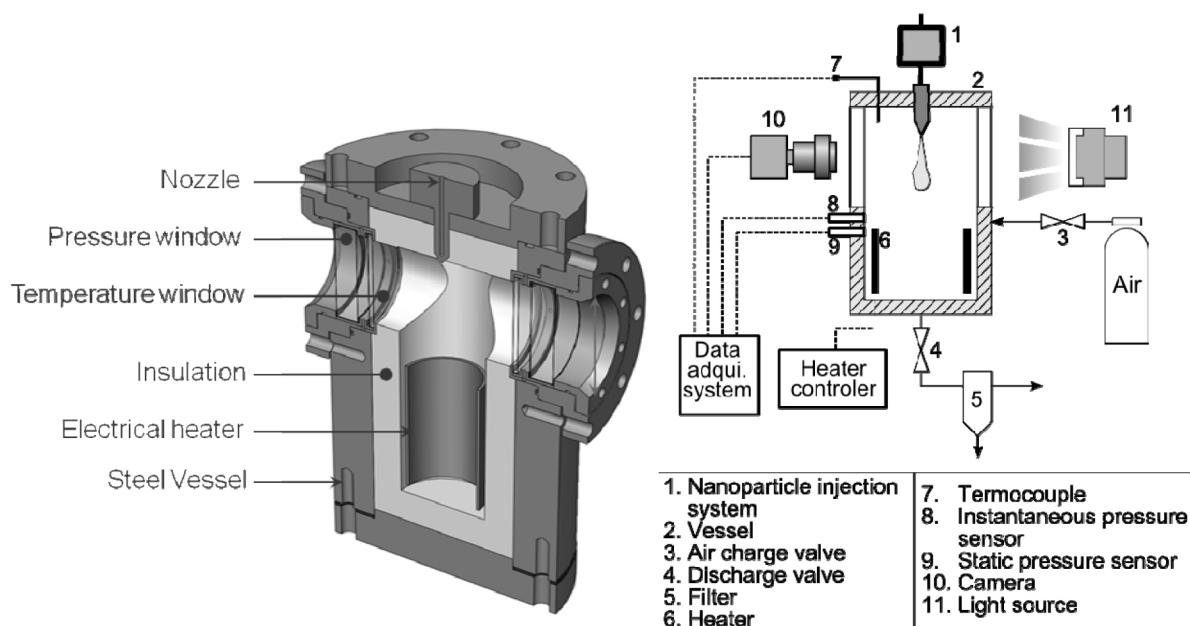


Figure 3. High-pressure, high-temperature constant volume test rig setup.

was used for combustion imaging; images were recorded at a rate of $4 \cdot 10^4$ frames per second using a Phantom V12.0 high-speed camera.

The engine set up is schematically shown in Figure 4 (picture on left). The main characteristics of the single cylinder compression-ignition ICE employed in the present study are reported in Table 2. The engine was instrumented with sensors for the required in-cylinder pressure and intake/exhaust line pressure/temperature measurements. Intake air flow was conditioned and measured by means of a custom-

made air feeding system. A simplified metallic powder feeding system was placed upstream of the intake valve runner (right picture of Figure 4). The feeding system is practically a nanopowder reservoir placed between a check unidirectional poppet valve and a solenoid valve, the latter connected with a low pressure (8 bar) nitrogen supply line. Each “shot” of powder, synchronized with intake valve opening, inducted inside the cylinder was of a quantity sufficient to perform at least one combustion cycle. The exhaust line was equipped with a particulate filter system for the collection of combusted particles downstream of the engine.

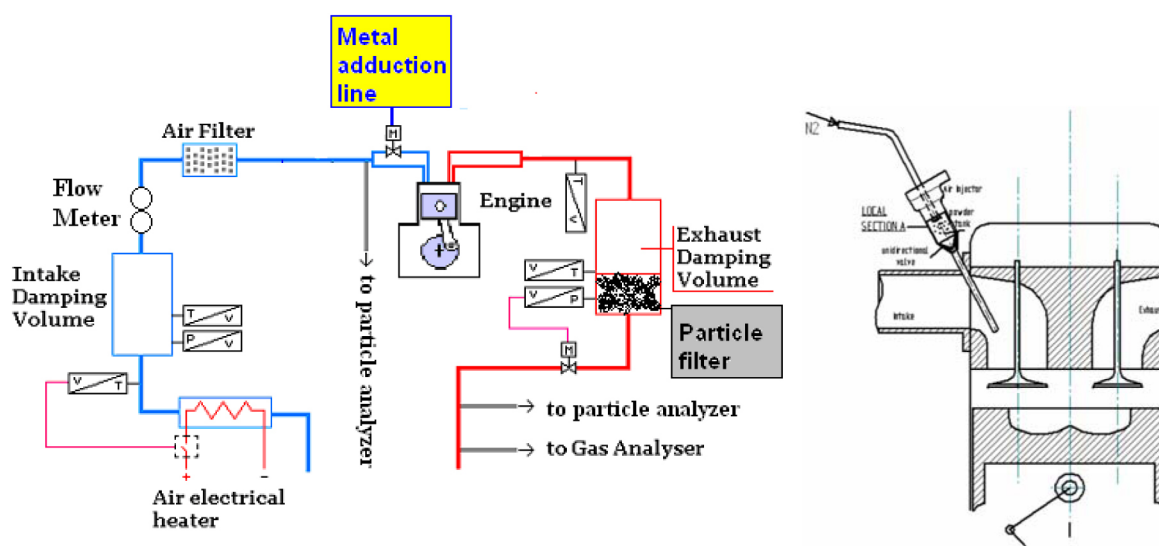


Figure 4. The first engine set up utilised for the studies of metallic nanoparticles combustion (left) and the nanoparticles injection system in the intake duct (right).

Table 2. Main characteristics of the engine utilised for the metallic nanoparticles combustion studies.

Property	Value/Description
Engine type	Single-cylinder Lombardini SP 15 LD 350
Displacement	350 cc
Bore/Stroke/Conrod length	82/66/110 mm
Compression ratio	20.3
Cooling system	Air

RESULTS AND DISCUSSION

1. TGA STUDIES

Each of the three different types of metallic nanopowder was initially subjected to TGA analysis under O_2 , O_2/N_2 and N_2 atmospheres in order to evaluate their fundamental oxidation and/or nitridation characteristics. The respective curves are shown in [Figure 5](#).

In the case of the iron nanopowders, it was evident that as the O_2 content decreased the oxidation rate decreased, too. The effect on Fe50 was moderate, while for Fe85 there was a profound difference between the pure O_2 or air cases and that of 2% O_2/N_2 . The in-house Fe85 nanoparticles were more readily oxidised, despite the fact that their Average Primary Particle Size (APPS) was higher. More specifically, the oxidation of Fe85 started at circa 390 K and was essentially complete by 570 K while in the case of Fe50 the respective temperatures were approximately 420K and 780 K. The higher reactivity of Fe85 could be ascribed to its higher degree of agglomeration (as shown in [Figure 1](#)) that facilitated faster propagation of the oxidation process via the mechanism of heat conduction between the particles of each cluster. Furthermore, due to their irregular shape, the Fe85 nanoparticles had a larger area of contact with the surrounding oxidising gas, as compared to that of the almost spherical Fe50 particles. The total weight increase observed for both Fe nanopowders was close to the respective calculated theoretical values of 38-39.5%wt (shown in [Table 1](#)). The slight weight increase observed under N_2 was attributed to a (limited) leakage of ambient air into the tank containing the powder during the particular experiment.

On the contrary, in the case of O_2/N_2 mixtures, Al50 nanoparticles revealed two distinct weight increase temperature windows. The first one, corresponding to the steep weight increase in the range of 770-820 K, was attributed purely to metal oxidation (formation of Al_2O_3).

The second phase of weight increase (range of 970-1270 K) was mainly attributed to the nitridation reaction (AlN formation) that proceeded at a distinctively slower rate. The oxidation ignition temperature was in fair agreement with the relevant findings reported in [7, 8]. The overall trend suggesting the occurrence of two different reactions in the Al case was apparently confirmed by the shape and respective temperature ranges observed for the TGA curves obtained under pure O_2 and pure N_2 atmospheres. It is also important to note that, as the O_2 content decreased the oxidation rate of Al50 was slowed down to an extent that was much more profound than that observed in the iron nanoparticles case. The latter is essential in the process of controlling combustion by means of exhaust gas recirculation (EGR).

Shown in [Table 3](#) is an overview of the products obtained during the TGA experiments of the Fe and Al nanopowders, based on the respective XRD spectra of the 'spent' (subjected to TGA) samples. The identified phases are written in descending order with respect to their intensity in the XRD patterns. Clearly, for reactant mixtures containing O_2 , Fe50 and Fe85 were completely oxidised to Fe_2O_3 , while in the case of Al50 the phases identified in XRD were Al_2O_3 , AlN as well as a notable quantity of unreacted metal. Justification of the presence of the metallic phase could be attributed to the fact that the Al powder in direct contact with the gaseous stream was either oxidised or nitridated as temperature increased, while at temperatures exceeding 930 K the remaining metal melted. The AlN and Al_2O_3 formed remained in the solid phase, eventually growing to form a thick and relatively dense layer that isolated the liquified Al 'core' from the gas flowing over the powder container.