# Ignition by Mechanical Sparks – Ignition Temperatures of Hydrogen/Air-Mixtures Ignited by Small Metal/Ceramic Particles

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## 1 Introduction

Cutting and reshaping processes like grinding and abrasive cutting can produce small hot particles – mechanical sparks. Also impacts can create sparks, e.g. a pick-axe on a rock. Mechanical sparks as ignition sources play an important role in safety-related assessments of the ignition of combustible mixtures [1]-[4]. They are generated by a short mechanical action on solid materials. In any case, mechanical sparks are separated, usually glowing individual particles, formed locally at the site of action. Depending on the generation process, the spark material and atmosphere, such particles might reach (surface) temperatures of up to about 2000°C [1]. As the particles fly through the ignitable gas mixture, their energy is dissipated to the surrounding by heat conduction and radiation. In that sense, sparks of non-combustible particles are somewhat similar to hot surfaces. However, owing to the large surface-to-volume ratio, often the energy dissipation is too large and too fast to ignite gas mixtures that would ordinarily ignite at self-ignition temperatures well below 1000°C [4].

Contrary to hot surfaces and electrical discharges, much less data is available on the ignitability of combustible mixtures by mechanical sparks. Previously, experiments have been performed with an emphasis on the amount of impact or friction energy at the site of action that eventually leads to ignition [1][3][4][5]. However, there is little known about the detailed ignition event at the hot particle itself. The ignition of fuel/air mixtures by small hot nanoparticles has been studied some authors in conjunction with irradiative cw-laser heating to obtain safetyrelevant critical laser powers that lead to ignition [6][7][8][9]. In those experiments, carbon black or metal-oxide nanoparticles were coated or deposited onto the tip of an optical fibre and illuminated by a cw-infrared laser. Hills et al. [10] and Zhang et al. [11] observed an increase in the required critical laser power with both the laser beam and particle size for the ignition of hydrogen/air mixtures by a single coal particle held at the end of an optical fibre. The effect was attributed to the rise in mass and, hence, thermal capacity with increasing particle size and the reduction of the radiation flux caused by the enlargement of the irradiated area at constant power. Stamatov et al. [12] showed ignition of methane/air mixtures for a single inert aluminium oxide particle using an argon ion laser as heat source. Recently, Beyer and Markus [13] monitored and simulated the surface temperature of artificial, laser-heated iron oxide particles at the time of ignition for different fuel/air mixtures. The minimum surface temperature of ignition increases strongly with decreasing particle size and is well above the autoignition temperature of the corresponding fuel/air mixtures, owing to the poor heat transfer from the spherical particles into the gas phase.

In this paper we investigate the ignitability of quiescent combustible mixtures ( $H_2$ /synthetic air) by a hot particle. The generation of the mechanical sparks will be neglected in favor of the experimental accessibility of spatially fixed single particles. A cw-argon ion laser will be used as heat source to heat up the particle. The effect of

particle material and size on the ignition temperature will be studied and compared with detailed numerical simulations.

# 2 Experimental Setup

To examine the ignition properties of mechanical sparks, an explosion proof vessel was built, having eight ports around its middle plane (Fig. 1) that provide mechanical or optical access for the particle manipulator, laser beam, pyrometer, as well as for a fast ICCD camera for OH\* imaging. Particles of different material and size are fixed on a very thin hollow needle (Ultradent EndoEze 31G,  $D = 250\mu m$ ,  $d = 150\mu m$ ) and placed in the optical focus of the pyrometer near the centre of the chamber. Connecting the needle to a vacuum pump, small particles can be securely attached to the tip of the needle. A cw-argon ion laser (Coherent Innova 70-C5, multiline operation, laser power 7.5W, 1/e<sup>2</sup> radius 0.64mm) is directed through a fused-silica window onto the particle. A plano-convex lens (f = 1000 mm) reduces the laser-beam diameter before hitting the particle 400 mm behind the lens, while the focal point is located outside the chamber. No ignition has been observed by directing the laser through hydrogen/air mixtures without a particle placed into the beam. The laser power was held constant at 4.5 Watts for the experiments. As the laser beam is still slightly larger than the particle, it leaves the vessel through the window on the opposite side, where it is sampled by a photodiode to determine the onset of heating and to verify stable laser power output. Explosive atmospheres were produced by intermixing the gas streams of two mass-flow-controllers (Brooks Instrument 5850E), which delivered a defined flow of synthetic air and hydrogen, in a one meter long mixing pipe before entering the ignition chamber. A proper setting of flow rate and purge time ensured a complete replacement of the atmosphere inside the chamber before the next experiment started. All experiments were performed at ambient pressure.



Fig. 1: Schematics of the ignition chamber (left) and of the optical path of the pyrometer (right).

A two-wavelength pyrometer was built for the experiments to monitor the surface temperature of laser heated particles with diameters in the sub-millimeter range (Fig. 1, right). The thermal radiation from the particle is captured by a large diameter aspheric lens (S-LAH64, f = 32mm, NA 0.612) and imaged through a set of planoconvex lenses and bandpass filters onto large area photodiodes (Thorlabs, PDA520). Our custom build pyrometer ensures a high collection efficiency of the thermal radiation and a very high stability with respect to the positioning ( $\pm 1$  mm) of the small particles. The pyrometer was calibrated against commercial type K (NiCr/Ni) and custom-made type S (PtRh/Pt) thermocouples, which were placed in the focus of the pyrometer and heated by different laser-powers to stationary temperatures.

The main scope of the project is to evaluate the ignition capabilities of small hot metal particles in hydrogen/air mixtures. However, to determine the influence of surface reactions, experiments with ceramic particles were also conducted using silicon nitride (Si<sub>3</sub>N<sub>4</sub>, spherical bearing ball,  $D = 800 \& 500 \square m$ ) and tungsten carbide (WC(Ni), nickel bonded, spherical bearing ball,  $D = 300 \& 800 \mu m$ ). Bearing balls made from three different steels (1.3505, 1.3541, and 1.4034) were used as targets with diameters between 400 and 800  $\square$  m, depending on commercial availability. In addition, more or less spherical but polydisperse shot-blasting particles made from casting steel (GS-R) and aluminum (5083) were used to verify the influence of the particle size on the ignition process. The sizes of the shot particles ranged between 600 and 1000  $\mu m$ , as measured by an optical microscope.

## 3 Numerical Model

Detailed numerical simulations were performed with our in-house numerical code (INSFLA). The unsteady conservation equations were formulated assuming spherical symmetry, quiescent ambience and steady pressure both in time and space. Detailed mass and energy transport was accounted for in both solid and gas phase as well as at the solid/gas interface. Neumann-type boundary conditions are defined for the species concentration and

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temperature at the outer boundary of the computational domain, with a gradient of zero, so that no heat or mass can be exchanged with the surroundings. Radiative heat loss from the solid particle to the ambience was modeled using Stefan-Boltzmann's law. The particles were assumed to be inert particles in the investigated temperature range (300K - 1400K) because of passivation [14]. The particles used have high melting temperature and sublimation temperatures hence, here we neglected vaporization of particles in present study consequently detailed chemical kinetics was accounted only in gas phase and only for species involved in H<sub>2</sub>/O<sub>2</sub> reactions. The detailed reaction mechanism of H<sub>2</sub>/O<sub>2</sub> combustion from Maas and Warnatz [15] with 9 species and 19 reactions was used to model the gas phase chemistry. The surface reactions were neglected due to the lack of reliable rate kinetics data on surface reactions in literature. The thermodynamic and transport data was taken from JANAF tables [17].

The resulting partial differential equation system was discretized by the method of lines using finite difference and solved using the linearly implicit extrapolation method (LIMEX). A more detailed description of the code and the governing equations is available in Stauch et al. [16].

### 4 **Results and Discussion**

Fig. 2 shows the surface temperature of different particle materials and sizes at the time of ignition for a 15/85% v hydrogen/air mixture at ambient pressure. A successful ignition event is characterized by a sudden increase of the surface temperature (heat release from the surrounding gas phase) and the development of an expanding flame front as monitored by OH\* chemiluminescence imaging. Among the different particle materials studied here, the chemically inert silicon nitride shows the lowest ignition temperature of about 900 K, while all metal particles require much higher temperatures. In addition, the ignition temperature increases with decreasing particle diameter for all but the aluminum shot particles. This increase is consistent with previous experiments and calculations on artificial iron oxide particles [13]. Both shot blasting materials (Fig. 2, right) are polydisperse in nature and do not have a perfect spherical shape, which is reflected in the scatter of the experimental values. All three steel materials show a similar trend, but have different ignition temperatures at fixed particle diameters. The steel types 1.4034 and 1.3541 refer to the same steel composition [18].



Fig. 2: Surface temperature at the time of ignition as a function of particle diameter for  $Si_3N_4$ , WC(Ni) and steel bearing balls (left) and for steel and aluminum shot particles (right) in a H<sub>2</sub>-Air 15-85%v mixture. The solid lines represent the prediction from the numerical model.

Also shown in Fig. 2 are the predicted temperatures at ignition from the numerical model (solid lines). The simulated values reproduce the general trend of increasing ignition temperature with decreasing particle size, but are otherwise rather insensitive to the particle material. The largely different ignition temperatures of the various materials are therefore not a result of different thermal properties, instead, they are most likely caused by surface reactions (e.g., radical quenching), which are not included in the numerical model yet. The tungsten carbide balls ignite the gas phase at significantly higher temperatures than the silicon nitride balls, which may be caused by quenching reactions of the nickel binder in the tungsten carbide. However, even the ignition temperature of the chemically inert  $Si_3N_4$  particles is overestimated by about 200 K. This overestimation could also be attributed to a lack of accurate data which follows from a wide range in data values found in literature.

Ignition experiments were also conducted using different gas-phase compositions, varying the hydrogen content between 5 and 40 %v. In Fig. 3 the surface temperatures at ignition are plotted against the hydrogen-content (%v) of the quiescent atmosphere in the ignition chamber. As in Fig. 2, smaller particles require higher

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temperatures to ignite the gas-phase. The only exceptions are the  $700\mu$ m particles made from 1.4034. Their heating curves flatten just before ignition, which results in a lower ignition temperature. The reason for that behavior is still unclear.



Fig. 3: Surface temperature at ignition for spherical particles as a function of the  $H_2$  content in air. The solid lines represent the prediction from the numerical model, the dashed line represents the autoignition temperature, values taken from [19]

With increasing hydrogen content the ignition temperature generally increases as well. This may be due to the fact that the thermal conductivity of the gas phase increases almost by a factor of two in the mixture range covered by the experiments. Thus, the energy in the gas-phase is dissipated more quickly in hydrogen-rich mixtures, leading to a higher necessary surface temperature to achieve ignition. Smaller particles ( $d \le 500 \mu m$ ) show a minimum in the temperature curve near 15%v hydrogen in air.

All measured ignition temperatures are above the autoignition temperatures of 800-900K described in literature [19], this is explained by the fact that autoignition temperatures refer to a mixture of homogeneous composition and temperature, whereas in our case the mixture is locally heated by a small particle.

A more distinct picture of the ignition capabilities of various small hot particles is obtained by comparing the overall energy (per unit volume) that has been deposited inside the particle until ignition occurs. It is defined as the integral over the heat capacity from ambient temperature up to the temperature at ignition. Thermal expansion and phase transitions will be neglected for now. On the time scale of the experiment, the temperature is assumed to be homogeneous over the particle core and equal to the detected surface temperature. The low Biot-number (Bi < 0.01) supports this assumption. CFD simulations of the cw-laser heating process show a maximum temperature drop of ~100 K from the irradiated side to the opposite side of the particle. Fig 4 illustrates the deposited energy density as a function of the particle diameter for hydrogen/air mixtures. The diagram contains points for all particle materials and mixture compositions. Multiple points at a given particle size correspond to different mixture compositions. Dashed lines represent the minimum energy densities for each material that will ignite the combustible gas mixture.



Fig 4: The amount of energy (per unit volume) deposited in the particle until ignition as a function of particle diameter in hydrogen/air mixtures.

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The minimum energy density decreases with increasing particle size, but differs in magnitude between the different particle materials and increases in the order  $Si_3N_4 \approx Al-5083 < WC(Ni) < 1.3505 < 1.3541/4034$  by a factor of two. For comparison, if we apply the same analysis to the data of Silver [20] then platinum particles require ~3.2 kJ cm<sup>-3</sup> and quartz particles ~2.6 kJ cm<sup>-3</sup> to ignite a mixture of 20% hydrogen in air (extrapolated to a particle diameter of 800 µm). Energy densities of aluminum shot blasting particles (Al-5083) are virtually independent of particle size (compare Fig 4). It is likely, that the thin aluminum oxide layer is responsible for the different behavior, but the details are yet unclear.

While Fig 4 nicely illustrates the differences between the various particle materials, we have no direct measure of the amount of energy that needs to be transferred to the gas phase in order to induce ignition. However, the



Fig 5: The amount of energy deposited in the "ignition relevant" gas phase volume  $(h_{gas})$  at the time of ignition as a function of hydrogen content and particle diameter. The gray, solid line represents the minimum ignition energy of hydrogen/air mixtures [21].

simulations of the ignition process in hydrogen/air mixtures provide one-dimensional spatial temperature profiles inside the particle and throughout the surrounding gas phase at the time of ignition. The modeled ignition temperatures in Fig 3 are then just the temperatures evaluated at the time of ignition and on the particle surface. For the gas phase, we can define an "ignition relevant" volume that spans from the particle surface up to the radial position  $r^* = r(T_{\text{self ign.}})$ , at which the gas phase temperature drops below the self-ignition temperature. Although choosing the relevant volume is somewhat arbitrary, it reflects the observation that temperatures below the self-ignition temperature are not sufficient for ignition. We can now evaluate the total energy that has been deposited in the gas-phase  $h_{gas}$  (at constant pressure) up to the time of ignition, by integrating the temperature dependent gas enthalpy from the particle surface to r\*:

$$H(r) = \sum_{i=H_2,O_2,N_2} x_i \int_{T_0}^{T_{gas}(r)} \frac{p}{RT} C_{p,i}(T) dT \qquad h_{gas} = 4\pi \int_{r_p}^{r^*} r^2 H(r) dr$$

Fig 5 shows the energy transferred to the gas phase  $(h_{gas})$  as a function of mixture content and particle diameter. Generally, the energy increases with increasing hydrogen content and with increasing particle diameter. The latter effect is simply due to a decreasing curvature with increasing particle size, while the first effect reflects the higher thermal conductivity in hydrogen rich mixtures and, thus, an increase in  $r^*$ . The gas phase energies are of similar order of magnitude as the minimum ignition energies of hydrogen/air-mixtures [21] (gray line in Fig 5), but do not reflect the sharp increase at the lower ignition limit. Dividing the energies  $h_{gas}$  by the "ignition relevant" gas phase volume, all curves collapse to a single constant line at an energy density of 0.25 MJ/m<sup>3</sup> that is independent of particle diameter and mixture composition.

Samples from all materials were taken before and after ignition experiments and analyzed with a Hitachi scanning electron microscope (SEM). The SEM was equipped with an EDX-detector, allowing elemental analysis of different surface regions of the samples. Whereas the metal particles visually showed annealing colors and superficial morphological differences, the SEM-EDX analysis did not show an andvanced degree of oxidation after ignition in an oxygen containing atmosphere. In most cases, the spherical bearing ball particles (Si<sub>3</sub>N<sub>4</sub>, various steels) remained essentially unaltered by the ignition experiment. In contrast, the steel shot sample (GS-R) showed a metallic phase below oxidic layers before the ignition event. After the experiment, the oxidic shell was cracked and partially peeled off, exposing the lower metallic layer (Fig 6). Aluminium particles showed no morphological changes upon ignition as well as no further oxidition, probably due to the passivation of aluminium.



Fig .6: SEM surface images of GS-R steel shot particles (a) before and (b) after ignition. Also shown are optical microscope images (inset).

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### 5 Conclusion

Particles made from different materials in different sizes were investigated concerning the necessary particle surface temperature to ignite a surrounding, quiescent hydrogen/air-mixture of different hydrogen/air-ratios. Experimental results show that smaller particles have to be heated to higher temperatures in order to achieve ignition. Aluminium particles showed no clear size dependency. Also higher hydrogen contents require higher surface temperatures to ignite the gas-phase. As different particle materials are concerned, they all require higher surface temperatures than  $Si_3N_4$  to ignite the gas atmosphere. Simulation results confirm the tendencies, but a further investigation of surface effects of different materials is necessary. Results indicate that energy density deposited in the particle might be a criterion to determine the success of ignition regardless of hydrogen-content and particle material. Also gas-phase energy in an "ignition relevant" volume can be used to compare the simulation results to minimum ignition energies.

### Acknowledgements

The authors gratefully acknowledge Deutsche Forschungsgemeinschaft DFG (FOR 1447) for its financial support. We thank Boris Reznik for taking the SEM images.

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