SENSITIVITY TO DETONATION AND DETONATION CELLULAR STRUCTURE OF H_2-O_2-AIR-H_2O_2 GAS MIXTURES

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ABSTRACT

Today it is not known – neither qualitatively not quantitatively - how large the impact can be of the promoters on sensitivity to hydrogen-air detonation in hypothetical accidents at hydrogen-containing installations, transport or storage facilities. Report goal is to estimate theoretically an effect of hydrogen-peroxide (as representative promoter) on sensitivity to detonation of the stoichiometric hydrogen-oxygen gas mixtures. The classical H_2-O_2-Ar (2:1:7) gas mixture was chosen as reference system with the well established and unambiguously interpreted experimental data. In kinetic simulations it was found that the ignition delay time is sensitive to H_2O_2 addition for small initial H_2O_2 concentrations and is nearly constant for the large ones. Parametric reactive CFD studies of two-dimensional cellular structure of $2H_2$-O_2-$7Ar$-H_2O_2 detonations with variable hydrogen peroxide concentration (up to 10 vol.%) were also performed. Two un-expected results were obtained. First result: detonation cell size is practically independent upon variation of initial hydrogen peroxide concentration. For practical applications it means, that presence of hydrogen-peroxide did not change drastically sensitivity of the stoichiometric hydrogen-oxygen gas mixtures. These theoretical speculations require an experimental verification. Second result: for large enough initial H_2O_2 concentrations (> 1 vol.% at least), a new element of cellular structure of steady detonation wave was revealed. It is a system of multiple secondary longitudinal shock waves (SLSW), which propagates in the direction opposite to that of the leading shock wave. Detailed mechanism of SLSW formation is proposed.

NOMENCLATURE

p	- pressure, Pa
T	- temperature, K
V	- velocity, m/sec
[CS]	- concentration of chemical species CS, vol.%
τ_{ind}	- induction time, sec
$_{max}$	- referred to maximal value
$_0$	- referred to initial conditions
$_{vN}$	- referred to von Neumann point

1.0 INTRODUCTION

1.1 Motivation

Detonation is one of the most hazardous effects, which is possible in fuel-air gas mixtures. Understanding and assessment of detonative properties of hydrogen-containing mixtures is a matter of great practical importance, especially in view of the coming transition to a hydrogen economy. Today, there exists an ample set of data on sensitivity to detonation for the H_2-O_2, H_2-O_2-Ar, H_2-O_2-He, H_2-O_2-N_2, H_2-air and H_2-air-steam gas mixtures [1], where the other then hydrogen and oxygen chemical species play, mainly, role of inert diluent. The hydrogen-containing gas systems with chemically active additions have been much less studied. For example, influence of the carbon monoxide additions on sensitivity to detonation for the hydrogen-containing mixtures is studied theoretically only [2]. The major part of this knowledge was obtained in studies devoted to hydrogen safety of nuclear power plants [3]. An influence of the chemically active additions (promoters) on detonative sensitivity of the H_2-O_2 gas mixtures is a scarcely studied topic. It appears that there are no experimental data for hydrogen-air mixtures with chemically active promoters. This omission is probably due to the difficulty in performing experiments involving promoters. They are, frequently, unstable and the highly toxic or explosive gases and require special precautions in handling and storage. Despite of the obvious difficulties in experimental studies of the hydrogen-containing gas mixtures in presence of combustion promoters, the extent and the mechanisms of impact of promoters on sensitivity to detonation needs to be studied at least for two reasons. From practical viewpoint, especially from the perspective of assessing the potential threats during a hypothetical hydrogen accident, it worth considering, since the potential combustion promoters are widely spread in modern life. Some of combustion promoters (like as ozone, nitrogen oxides, etc.) appear in small concentration in the atmosphere of large cities as result of the intrinsic atmospheric processes (smog formation) or home appliances (ozone generators). Other promoters (like as H_2O_2) are used as reagents in the industrial chemical processes, for medical purposes and for domestic applications (bleaching, washing). From academic viewpoint, gaseous hydrogen- promoter detonation is a whole class of practically un-explored systems.

1.2 Problem

From one hand, an addition of a strong oxidizer (for example, peroxide) is traditionally used to sensitize the combustion processes in different applications - for example, to control the ignition delay times in the propulsion systems [4]. Available experience permits to assume that addition of strong oxidizer (even in vanishingly small amount) can result in enhanced sensitivity to detonation of H_2-O_2 mixtures. On the other hand, today it is not known in detail – neither qualitatively not quantitatively - how large the impact can be of the promoters on sensitivity to hydrogen-air detonation in hypothetical accidents at hydrogen-containing installations, transport or storage facilities.

1.3 Goal and Objectives

The main goal of our computational and analytical studies was to contribute to a first theoretical estimation of an impact of hydrogen-peroxide addition on the sensitivity to detonation in the classical H_2-O_2-Ar (2:1:7) gas mixture. Hydrogen peroxide was selected as a model chemically active addition for two reasons. First, it is a representative example of the combustion promoters. Second, its gas-phase chemical kinetics is reasonably well known as a part of overall mechanism of hydrogen-oxygen combustion [5,6]. In order to attain the mentioned goal, the following technical objectives were posed: 1) to assess quantitatively a variation of induction time delay with variation of initial hydrogen peroxide concentration using detailed kinetic computations; 2) to evaluate detonation cell length dependence upon initial H_2O_2 concentration using two-dimensional simulations of detonation cell structure.

2.0 EFFECT OF H_2O_2 ON INDUCTION DELAY TIME IN Z-N-D DETONATION WAVE

As a first indicator of sensitivity to detonation, it was selected and numerically assessed an induction time delay just behind the shock wave inside of a 1D Zeldovich-Neumann-Doring detonation wave.

2.1 Computational Procedure

A quantitative assessment of induction time delay dependence upon initial concentration of hydrogen peroxide for the model stoichiometric hydrogen-air-argon gas mixture (H2:O2:Ar=2:1:7) was performed in the following way. The initial concentration of hydrogen peroxide was varied from 10^{-3} to 10 volume percents. The values of initial temperature T_0= 298 K and pressure p_0=6670 Pa correspond to experimental conditions in [7]. At first step, the post-shock gas conditions, such as temperature T_{vN} and pressure p_{vN} (so called, the von Neumann parameters), were calculated for the given initial conditions (initial concentrations $[H_2]_0$, $[O_2]_0$, $[N_2]_0$, and $[H_2O_2]_0$; initial temperature T_0 and pressure p_0) using thermodynamic code CJ (Chapman-Jouguet model) from the Chemical WorkBench® – integrated software for thermodynamic and kinetic modeling of the complex chemical reactions and chemistry-loaded technological processes [8]. Secondly, the induction time τ_{ind} (T_0 , p_0, $[H_2O_2]_0$) dependence upon initial concentration of hydrogen peroxide $[H_2O_2]_0$ was computed using zero-dimensional kinetic code CBR (Calorimetric Bomb Reactor) from the library of the kinetic solvers in Chemical WorkBench® [8]. Kinetic calculations were performed for the adiabatic, isochoric conditions. Induction time was defined as a time, corresponding to the inflexion point in the temperature curve (maximal gradient of temperature rise). Details of the reaction mechanism used in the induction time calculations were the same as those given by Marinov [9]. This mechanism was selected [10] among the other comparable multi-step schemes after an extensive validation procedure.

2.2 Computed Results

Ignition delay time dependency upon initial H_2O_2 concentration is shown in Fig.1 below.

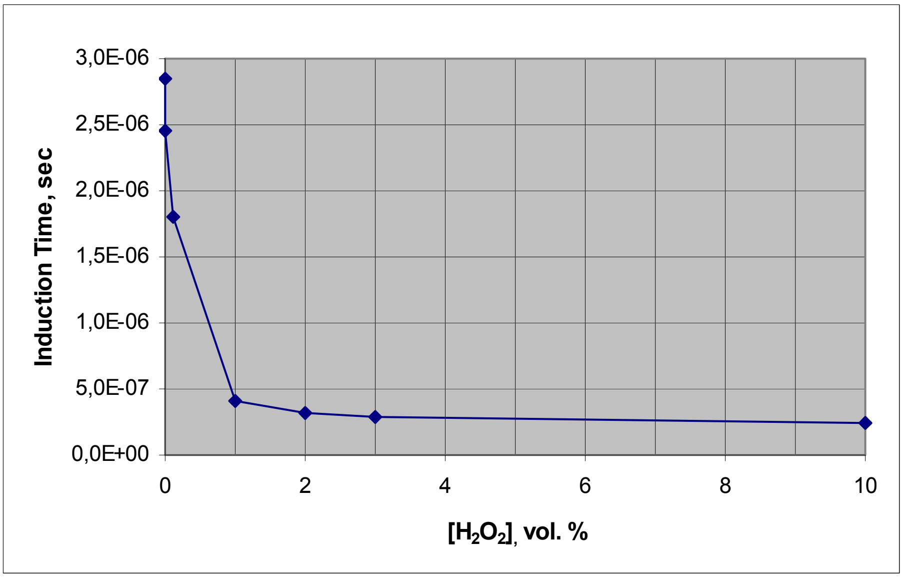

Figure 1. Calculated ignition time dependence upon initial hydrogen peroxide admixture concentration in 1D Z-N-D detonation wave (H_2:O_2:Ar=2:1:7, T_0=298 K, p_0=6670 Pa).

In kinetic calculations it was found that the ignition delay time behavior is sensitive to H_2O_2 addition for small (less then 1 vol.%) initial H_2O_2 concentrations and is nearly constant for the large ones. If correlation between induction time and detonation cell size should be a linear function, it may be to expect that admixing of more then 1 vol.% of hydrogen peroxide should decrease a detonation cell size by one order of magnitude in comparison with the pure hydrogen-oxygen-argon mixture.

3.0 CELLULAR DETONATION STRUCTURE IN PRESENCE OF H_2O_2

As a second indicator of sensitivity to detonation, the detonation cell sizes (width and length) were estimated using parametric numerical studies of the two-dimensional (2D) cellular structure of H_2-O_2-Ar-H_2O_2 detonations with variable hydrogen peroxide concentration (up to 10 vol.%).

3.1 Computational Procedure

The 2D computations of cellular structure were performed in reactive Euler approximation using the CADYC code [11]. This code was developed for the shock and detonation wave dynamics studies. It was recently ported to the massively parallel hardware MVS-1000. The here reported computations were performed on 70 processors. As well as in the kinetic simulations, the Marinov's scheme [9] was used for ignition chemistry modeling. Simulations were executed for rectangular Cartesian domain with transversal size 0.06016 m and longitudinal size 0.3072 m or 0.6144 m (in the last case the size of the numerical mesh have been doubled). The numerical meshes comprised 1024*128, 2048*256, 4096*512 nodes (as well as in [12]). The 2D computations were initialized by a few high-pressure zones of unburned reactive mixture. In Fig.2, a schematic drawing of the initial perturbation with the three high-pressure ($1000p_0$, p_0=6670 Pa), high-temperature ($25T_0$, T_0=298 K) zones (black color) is shown.

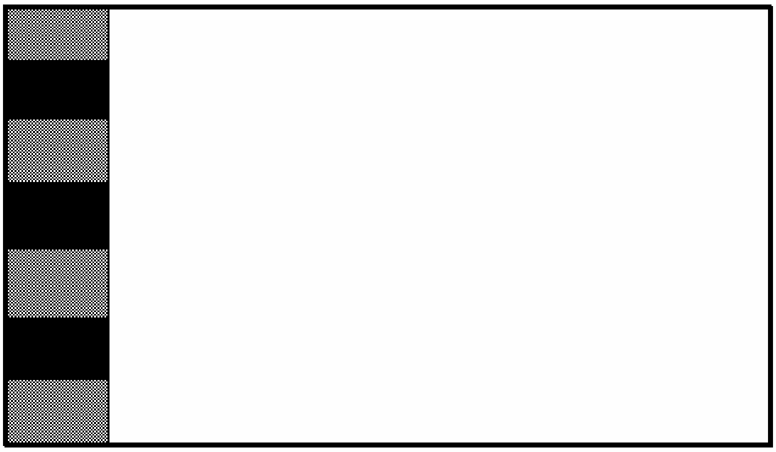

Figure 2. Initial pressure and temperature perturbation used to trigger 2D detonations waves propagation from left to right. (black zone – ($1000p_0$(atm), $25T_0$(K)), grey zone – (p_0(atm), T_0(K))

After elapse of a transition period of time, the self-sustained detonation waves with the same regular cellular structure were obtained for various number of disturbance zones and of initial values of pressure and temperature inside of them. Reproducibility of the steady cellular structure during the numerical computations with different initial disturbance parameters can be interpreted as independence of the final cellular structure upon initial conditions. Visualization of the computed results were performed using the 1) isolines for the all gasdynamic variables; 2) the maximum values of flow velocities on all grid nodes for given time moment $|V|_{\max,i,j} = [\sqrt{u^2+v^2}]_{i,j,\max}$ - to simulate the smoke foil tracks; 3) transformation $F = 0.8\exp(-30\nabla f / |\nabla f|_{\max})$ - to simulate the Schlieren photos of a physical variable f.

3.2 Computed Results

3.2.1 Triple Point Tracks

As a first step, a simulation of the cellular structure for classical $2H_2+O_2+Ar$ gas composition was made (see Fig.3)

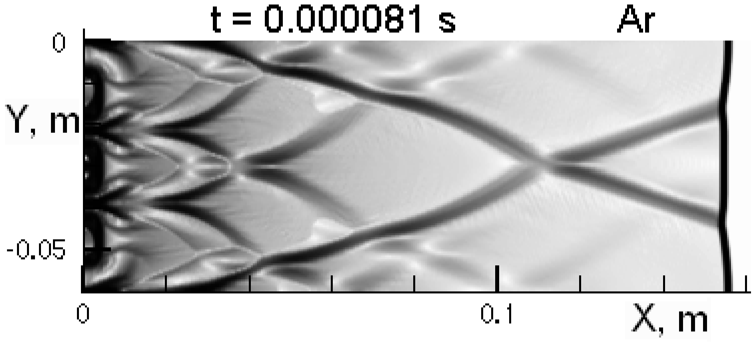

Figure 3. Fragment of detonation wave cellular structure for $2H_2+O_2+7Ar$ gas mixture (T_0=298 K, p_0=6670 Pa)

It was found, that the longitudinal size of detonation cell is 0.078 m. This value corresponds to the numerical results of previous works [12-14]. Secondly, the cellular structures of detonation waves were computed for hydrogen-oxygen-argon gas mixture with hydrogen peroxide admixtures. As an example, in Fig.4 a typical spatial pattern of cellular detonation structure for the $2H_2+O_2+7Ar+1.1111 \cdot H_2O_2$ gas mixture is shown.

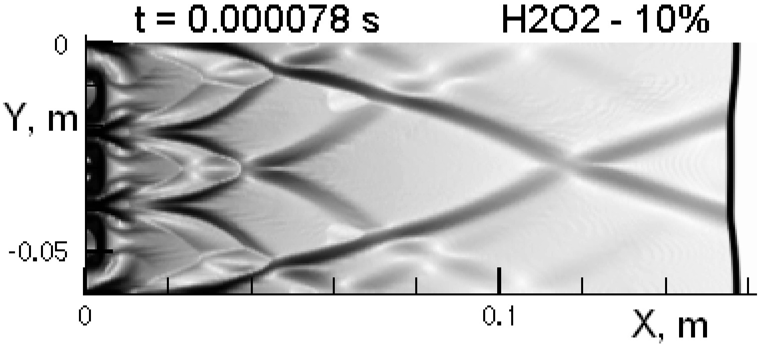

Figure 4. Fragment of detonation wave cellular structure for $2H_2+O_2+7Ar+1.1111 \cdot H_2O_2$ gas mixture (T_0=298 K, p_0=6670 Pa)

From Fig.5 it is seen, that admixing of H_2O_2 did not result in noticeable change of cellular structure. An analogous result was obtained for $2H_2+O_2+7Ar$ gas mixture with 1 vol.% addition of H_2O_2. On the basis of the numerical results obtained it can be concluded, that variations of initial concentration of H_2O_2 result in much more larger variations of induction time, then variation of detonation cell size. This fact can be regarded as an additional example of a complex and non-linear nature of correlation between detonation cell size and induction time. An unexpected result – practically invariant values of detonation cell sizes along with a large variation of induction times for hydrogen-oxygen-argon gas mixtures with hydrogen peroxide additives – forced us to analyze in detail the internal structure of detonation waves in hydrogen peroxide-containing mixtures, especially in the areas in vicinity of the triple points.

3.2.2 Secondary Longitudinal Shock Waves

For large enough initial H_2O_2 concentrations, within the well-known cellular structure of steady detonation wave a new element is emerging. It is a system of multiple secondary longitudinal shock waves (SLSW), which propagates in the direction opposite to that of the leading shock wave. As an example, in Fig.5 the 2D pressure field and the 1D profile p(X*)* at fixed transverse coordinate Y=0.0261 m are shown for the $2H_2 + O_2 + 7Ar$ gas mixture with 1 vol.% of H_2O_2.

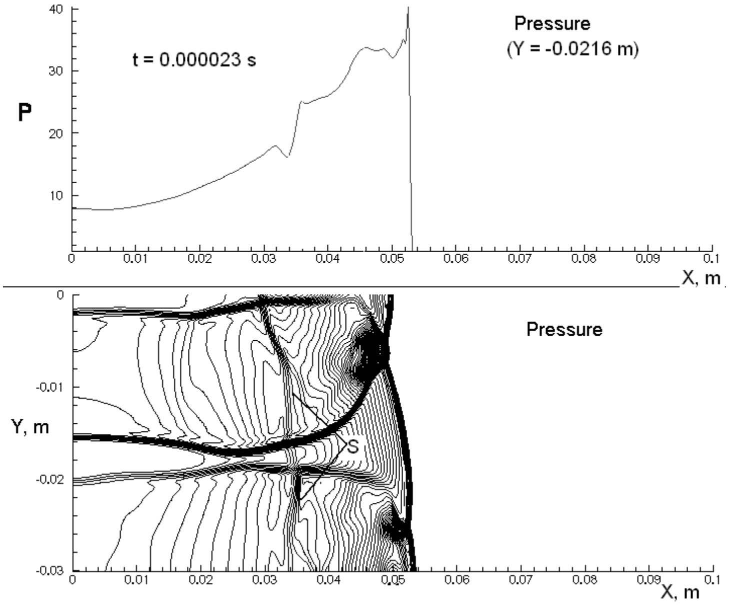

Figure 6. Secondary longitudinal shock waves are detached from leading shock waves

In Fig. 5, the two secondary longitudinal shock waves, originated in the two triple points (see Fig.6 below), are already detached from the leading shock front and cover the whole channel cross-section.

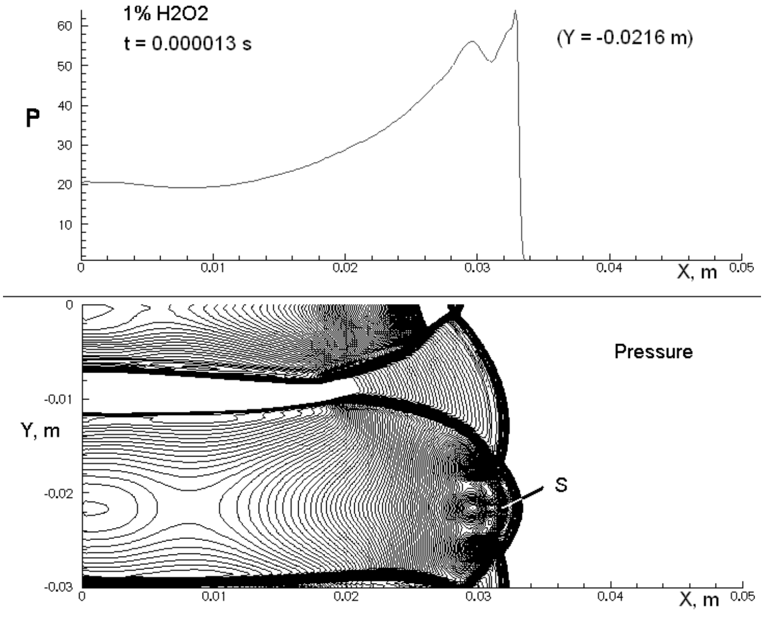

Figure 7. Secondary longitudinal shock wave is just formed behind leading shock waves

3.2.3 Mechanism of Secondary Longitudinal Shock Formation

Analysis of the SLSW evolution by "zooming" the spatial domains in the vicinity of the triple points (see Fig.7 below) supports the observation, that the secondary shock wave is forming as a result of "catching up" interaction of wave S_4 with leading shock wave D_2 (see Fig. 8a).

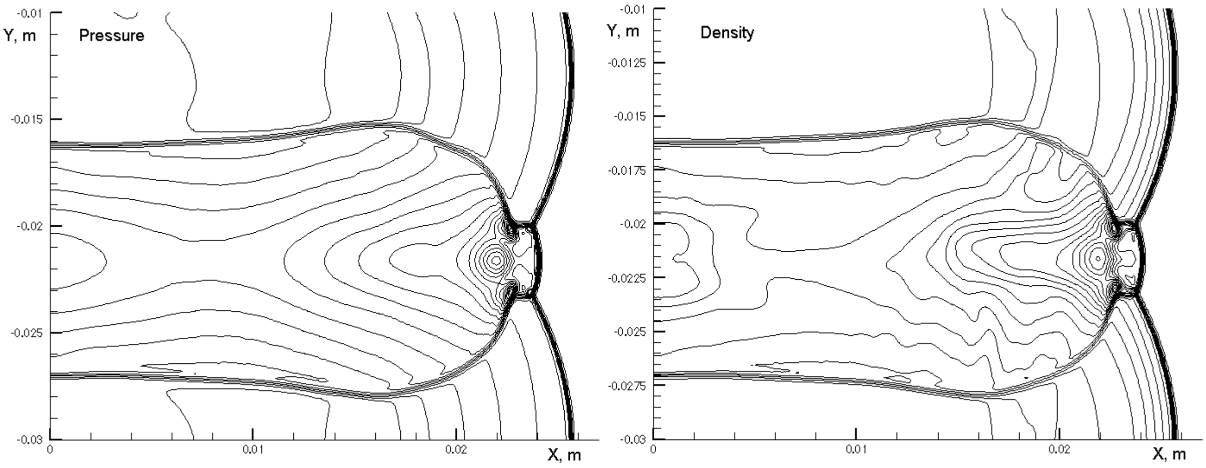

Figure 8. "Fine grain" structure near triple point collision of detonation cell

The mentioned type of non-regular, "catching-up" interaction of the shock waves [15] is characterized by the presence of the five shock waves S_1, S_2, D_1, D_2, S_3, two contact discontinuities C_1, C_2 and rarefaction wave *W* (see Fig 8a). Gradually, this non-regular intersection of shock waves is transformed into the simple Mach's interaction of the shock waves (Fig.8b). The simple Mach's interaction is realized away from the leading vertex of detonation cell. At the same time, the interaction of the contact discontinuities C_2 results in the formation of a vortex structure *R*, which is schematically shown in Fig.9 and Fig.10.

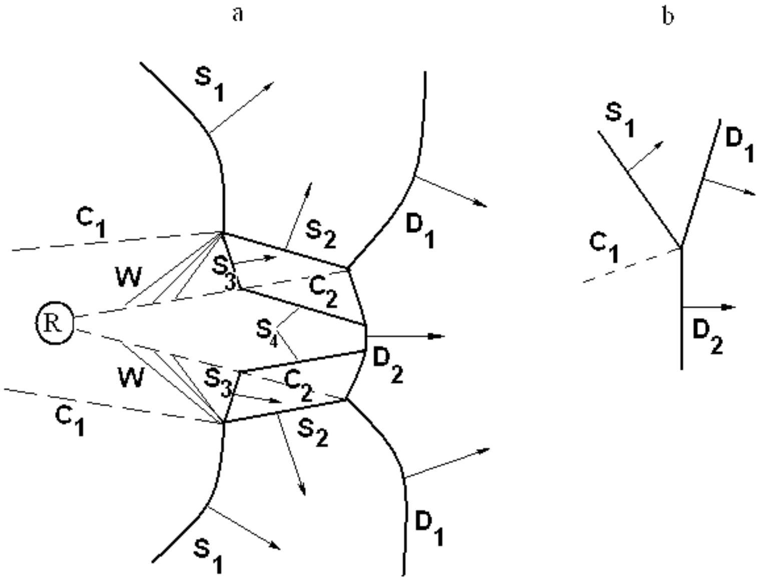

Figure 9. Two possible types of "catching-up" interaction of shock waves [15]

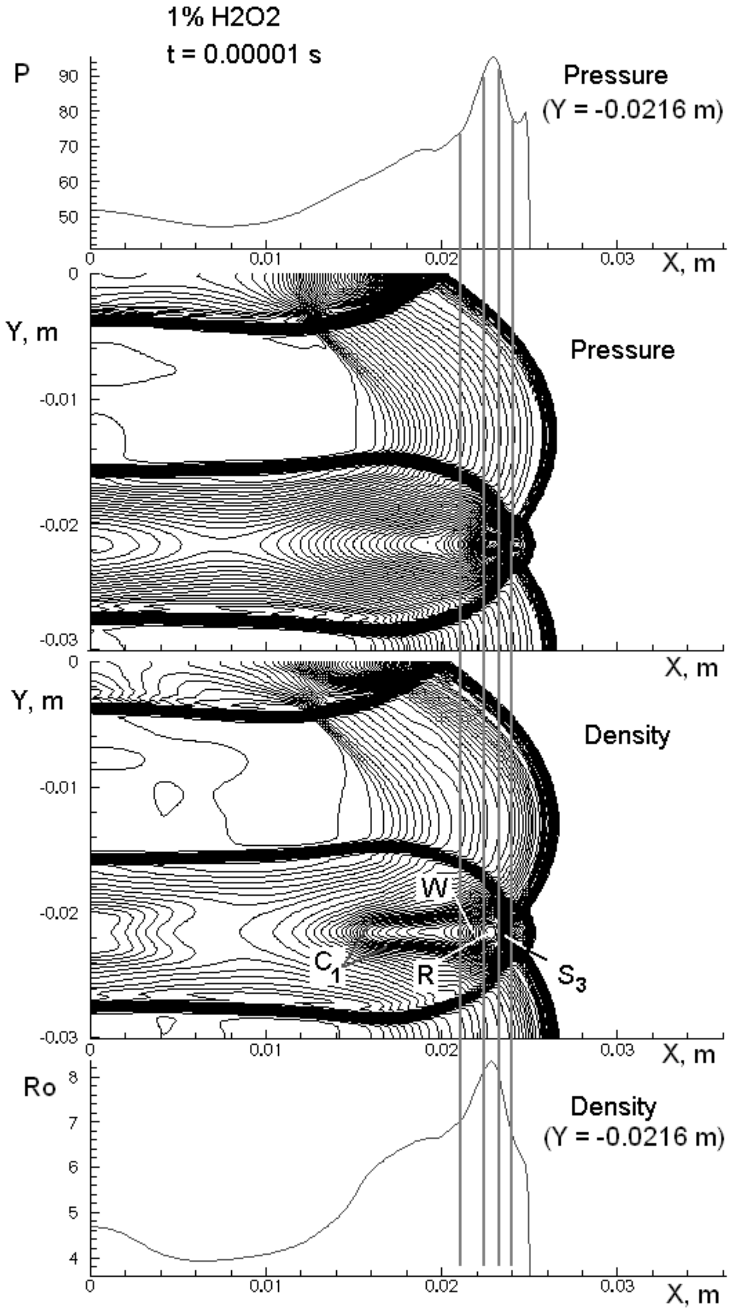

Figure 10. Pressure and density profiles and fields for $2H_2 + O_2 + 7Ar$ gas mixture with 1 vol.% of H_2O_2 at 0.00001 sec. ("Coarse grain" structure near triple point collision of detonation cell)

4.0 CONCLUSIONS

1. The problem of the risk of hydrogen detonation in the presence of the combustion promoters is introduced and is briefly discussed from the hydrogen safety and fundamental points of view. Promoters, specifically the strong oxidizers, are widely spread in modern life. As the chemically active species, promoters can, in principle, increase sensitivity of the hydrogen-containing gas mixtures to detonation. At present, knowledge is absent on where (critical conditions) and how (extent and mechanisms of influence) the promoters can increase the frequency of and aggravate the consequences of hydrogen detonation in a hypothetical accident. Experimental data on detonation cell size for hydrogen-containing gas mixtures with small admixtures of promoters are lacking. In this situation,

the analytical and numerical studies of the mentioned issue presently are the only means, capable to contribute to a preliminary answer to the question whether – could the combustion promoters change the risk of hydrogen detonation ?

2. The effect of small admixtures of hydrogen peroxide (as model combustion promoter) on sensitivity to detonation of $2H_2+O_2+7Ar$ gas mixture was evaluated theoretically using the kinetic and 2D reactive CFD simulations with a detailed chemical reaction model.

2.1 In the kinetic simulations, the ignition delay time dependencies upon initial temperature (900 – 3000 K), pressure (10^2-10^7 Pa), equivalence ratio (0.1-6.7) and H_2O_2 (10^{-3}-10 vol.%) fraction were estimated for adiabatic, isochoric conditions. For stoichiometric mixture, presence of small (1 vol.%) admixtures of hydrogen peroxide decreases substantially (around one order of magnitude) ignition time. For the post-shock conditions (von Neumann point in ZND detonation), it was found that the ignition delay time is sensitive to H_2O_2 addition for small (<1 vol.%) initial H_2O_2 concentrations and is nearly constant for the large ones. The decrease of induction time is higher (more then order of magnitude) for the off-stoichiometric mixtures.

2.2 The 2D CFD simulations (reactive Euler) of the cellular detonation structure in stoichiometric $2H_2+O_2+7Ar$ mixture have been performed with variation of initial hydrogen peroxide concentration. Two un-expected results were obtained. First, detonation cell size is practically independent upon variation of initial hydrogen peroxide concentration. Second, for large enough initial H_2O_2 concentrations (> 1 vol.% at least), a new element of cellular structure of steady detonation wave was revealed. It is a system of multiple secondary longitudinal shock waves (SLSW), which propagates in the direction opposite to that of the leading shock wave. A detailed mechanism of SLSW formation is proposed.

3. A decisive experiment on impact of combustion promoters on hydrogen detonation cell size is required. For effective experimental planning, the 2D estimations of detonation cell size in the off-stoichiometric H_2-O_2-Ar-H_2O_2 gas mixtures are necessary.

5.0 ACKNOWLEDGMENTS

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