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INFLUENCE OF VARIOUS TYPES OF AL_2O_3/MN_XO_Y CATALYSTS ON PERFORMANCE OF A 100 MM CHAMBER FOR DECOMPOSITION OF 98 %+ HYDROGEN PEROXIDE

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Abstract

The paper presents results of research on the catalytic decomposition of 98 % hydrogen peroxide, using special structures called composite catalyst beds. Such configuration of a catalyst bed can be applied in future green monopropellant thrusters for attitude control systems as well as self-ignitable and restart-able bipropellant engines.

A number of catalyst samples, based on aluminum oxides as support and manganese oxides as the active phase, were prepared for testing of catalyst decomposition of 98 %+ High Test Peroxide. The aim of the current stage of the test campaign is to select the most promising candidates for further research on 50 mm long chamber. The selection is made on the basis of hot test results in which dynamics of decomposition is evaluated. The other criterion is the structural integrity of the catalyst, assessed after the hot test. Support that is susceptible to cracking cannot be qualified as applicable for the next stage of the investigation.

The current research has shown that the crucial factor for performance of a catalyst is its specific surface area. The fastest pressure and temperature buildup has been reached for micro-porous γ-Al_2O_3 pellet.

Keywords: space propulsion, hydrogen peroxide, catalytic decomposition.

1. INTRODUCTION

The project managed in the Institute of Aviation is a part of the Green Propulsion Development Program. It was initiated as a response for changing trends in the field of space propulsion. Since hydrazine and it derivatives were placed on the European list of chemicals of very high concern (REACH – Registration, Evaluation and Authorization of Chemicals) [5], the space industry started to look for alternatives in case hydrazine is completely forbidden. Furthermore, any new component for propulsion, based on hydrazine, require special infrastructure for test activities, that is necessary to ensure safety for personnel and environment. Because of high cost of such facilities only large companies can afford to develop hydrazine propulsion. European industry stands for the exemption of propellant-use of hydrazine from REACH authorization requirement [1]. However, looking for alternatives is one of important development directions of European space industry.

Green Propellants seem to be very interesting option for new players, who want to bring innovative solutions into the field of space propulsion systems. Among green propellants that can be applied to monopropellant thrusters, several chemicals seem to be very interesting. These are: LMP-103S [4], AF-M315E [14] and HTP [15]. The first two propellants are based on highly explosive materials. It is even possible to recover explosives from these propellants by vaporization of solvents. HTP is the propulsion grade of hydrogen peroxide.

In Europe it is believed that HTP is the most promising green propellant [15]. It can be used for both mono- and bi-propellant applications. Peroxide is available in Europe for concentrations up to 90 %, with proper restrictions [6]. As 60 % water solution it is offered by most of chemical stores. It can be simply distilled in order to meet HTP parameters. Since performance of a propulsion system depends on concentration it is suggested to utilize HTP of the highest grade. According to the most approved standard for HTP – MIL-PRF-16005F, the highest grade is Type 98, which is 98 to 99 % high purity hydrogen peroxide [12].

2. CATALYSTS

The critical technology for propulsion, based on 98 % HTP, is the catalyst for its decomposition. Pure silver is not applicable since its melting point almost covers with decomposition temperature of 98 % hydrogen peroxide (940 °C) [7, 18]. Very interesting alternative seems to be platinum supported on metal-ceramic wire mesh (Fig. 1). According to test results such structure has good mechanic properties. However, cold-start characteristics are poor mainly because of low surface area and short residence time [11, 16].

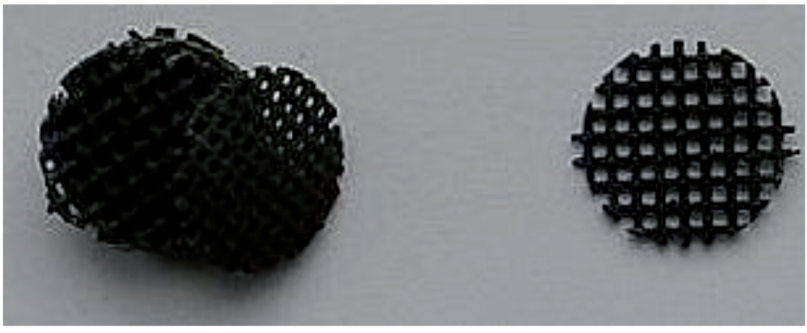

Fig. 1. Platinum catalyst supported on steel-ceramic wire mesh, manufactured by Catator [Author, 2014]

A number of ceramic supports, based on aluminum oxides, with various shapes and sizes can be covered by manganese oxides, using advanced impregnation techniques (Fig. 2). Manganese oxides have a strong catalytic effect on hydrogen peroxide [3, 8, 9, 11] and, by impregnation and calcination, create a stable connection with thermal resistant aluminum oxides.

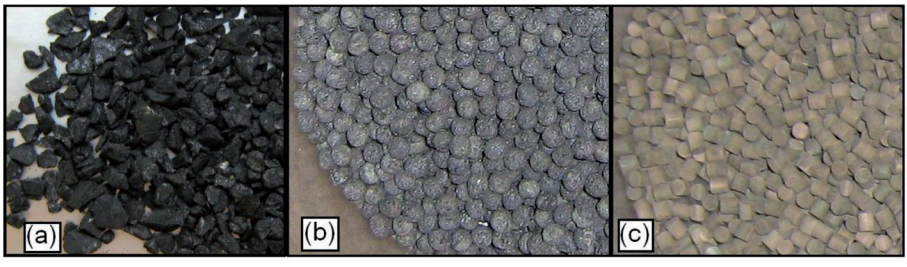

Fig. 2. Catalyst samples on various types of support: a – irregular pieces, b – spheres, c – pellets [Author, 2014]

Decomposition of hydrogen peroxide on ceramic supported catalysts is widely described in available references. Results of the experimental evaluation of several types of active phase (Mn_xO_y, Pt, Ru, Pd) impregnated on γ-alumina is illustrated in [2] as a qualitative analysis. According to this reference the order of various types of catalysts by means of their activities is as follows: Pt/Al_2O_3, RuO_2/Al_2O_3, Pd/Al_2O_3, Mn_xO_y/Al_2O_3.

However, these tests have been performed with 30 % hydrogen peroxide and the maximum concentration of H_2O_2 considered by authors of this paper is 87.5 %. The temperature of decomposition of 98 % peroxide is 260 °C higher that 87.5 %. That makes a difference especially considering structural matters (thermal shocks and a catalyst bed structural integrity). Moreover, since green space propulsion became an interesting alternative for commonly used hydrazine-based engines, 98 % peroxide have stayed hardly available on the global market. As a result, the current state of art for HTP decomposition catalysts is based mainly on experiments with PROPULSE 875 which is 87.5 % hydrogen peroxide produced by German manufacturer Evonik GmbH.

All catalysts used in the presented research are prepared in-house – using the Catalyst Preparation Stand. It was created under the project founded by ESA [10]. Ceramic particles (α- and γ-Al_2O_3) in the shape of spheres, pellets and irregular pieces are weighed at first and impregnated (by wet impregnation) with water solution of potassium permanganate with or without certain additives, such as oxides of: iron, samarium, chromium, lanthanum. After impregnation they are calcined in a high-temperature oven (600 - 700 °C). After cooling down and shaking they are weighed again in order to assess the mass of active phase that bound to the support. Weighing is the only method applied in the current research performed to evaluate the active phase content. Advanced methods of morphology assessment (i.e. SEM, EDAX, TEM) was not available at this stage of investigation.

According to [2] there are better solutions for decomposition of HTP than manganese oxides. The decision of selecting this chemical rather than precious metals and their oxides was mainly cost-driven. Moreover, at this stage of investigation the critical step was examination and selection of support which not only gives the highest performance but also withstands tough chamber conditions. In the opinion of the author this is the right choice for such early stage of research.

3. COMPOSITE CATALYST BED

The aim of research, founded by the European Space Agency, is to create and test special configurations called composite catalyst beds. The name composite is connected to the structure of the bed – with zonal distribution of ceramic pellet catalyst, separated by steel-ceramic-platinum wire mesh (Fig. 3).

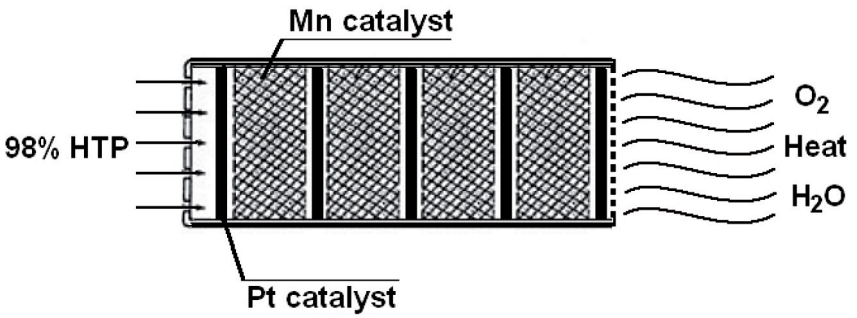

Fig. 3. Composite catalyst bed scheme [17]

In the author's opinion this structure should combine advantages of various types of catalyst, such as: good mechanical properties, high activity, good cold start characteristics, lifetime. 52 various catalysts were prepared to be tested. As many as 10 types of support are employed. These are spheres, pellets and irregular pieces, made of α and γ aluminum oxides.

All catalysts are tested in a thruster configuration, using 98 %+ HTP (Fig. 4). The alternative research method, presented in [2], uses a test rig, consisting of: a glass bottle (in which decomposition occurs) equipped with connections, pipette for peroxide application, glass tube, condenser, condensation separator and measurement equipment. Flow rate of gaseous oxygen is used as the basis to determine the reaction rate. Although this approach is simple and low-cost, it may be used for relatively low concentration of HTP. This method ensures data for comparison of various catalysts by means of the reaction rate with hydrogen peroxide. The approach presented in the paper, apart from ensuring comparative quality, represents real environment of rocket propulsion, which is the designed application for presented research.

The catalyst bed loading, selected for the research, is 40 kg/m^2/s. The general rule is that the higher bed loading the higher pressure drop (for the same size and shape of particles), better starting performance and shorter life time. The design loading is an intermediate value for different practical applications. In the case of monopropellant thrusters it may be even below 20 kg/m^2/s. For bi-propellant engines, depending on application, the bed loading range may be from 50 to even 200 kg/m^2/s.

The propellant is made of 60 % peroxide in the special laboratory unit, which was invented and built in the Propellant Laboratory of the Institute of Aviation [19]. According to lab test results, the purity of IoA's HTP is superior over the MIL-PRF-16005F standard.

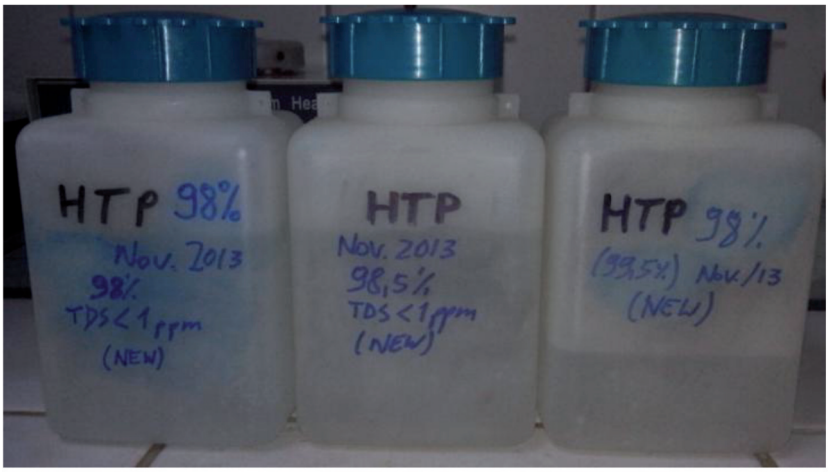

Fig. 4. Samples of 98 %+ HTP [Author, 2014]

The catalyst chamber, presented in the Fig. 5, was designed in a modular manner in order to ensure the possibility of re-configuration whenever necessary. It consists of: Ventouri, inlet manifold, injector plate, casing (diameter: 26 mm, length: 100 mm), aft support plate, outlet manifold and nozzle. Measurement ports along the chamber are included. Ports are located: 20 mm, 50 mm and 80 mm downstream of the injector plate. The catalyst bed is designed for chamber pressure 10 bar and volume flow rate 15 cm^3/s.

The shower head type injector has been selected for the catalyst bed. Due to the structure of the bed (fully filled with ceramic particles and wire mesh screens, no distance between the

injector and the first screen) the influence of a type of injector on decomposition phenomena may be, in general, neglected. Liquid jets entering into the chamber impinge on solid elements of the bed and instantly split, regardless of the type of injection. More important factor is a uniform distribution of peroxide on the cross section area. It is difficult to reach by the use of a single-jet injector. In the presented case the uniform distribution of the propellant was reached by calculating the arrangement of individual holes on the injection plate.

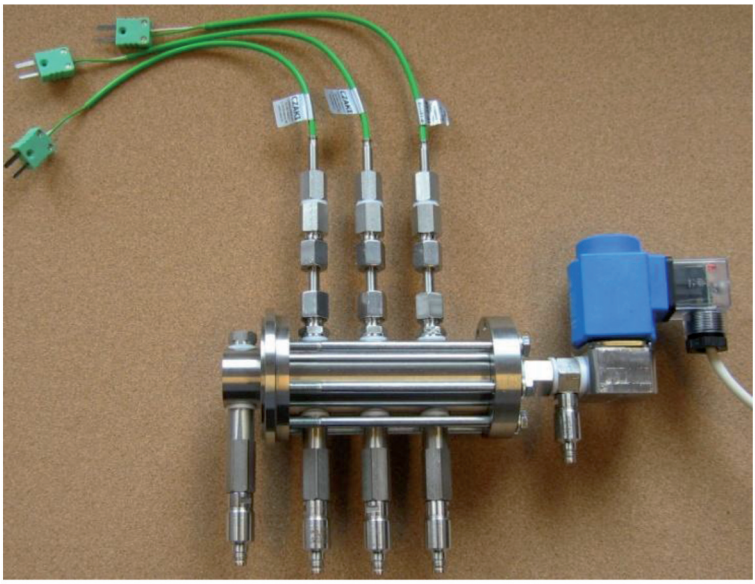

Fig. 5. 100 mm catalyst chamber in a thruster configuration [17]

4. TEST CAMPAIGN

The assumption was to evaluate dynamics of parameters change for each catalyst sample. The rate of temperature and pressure build-up at the aft end of the catalyst chamber gives the information how fast a thruster is able to reach its normal work. Maximum temperature for a single flow time specifies the quality of decomposition. Quality might be also determined by visual observation of the outflow. As long as the fume is visible, decomposition is poor.

Each sample is tested using the same hardware as well as inlet pressure in order to ensure repeatable conditions and to exclude possible discussion on the influence of various factors on the decomposition phenomena. At this stage of research, where just the general selection of catalyst candidates for further research is conducted, each sample is tested only one time (using defined test sequence). More detail investigation is planned to be performed at the next stage.

Numerous short pulses are introduced rather than long steady-state flows. To ensure data for comparative analysis, all tests are conducted using the same flow sequence and operating conditions. During the current phase of research all samples are tested in 100 mm long chamber. Temperature and pressure are measured at three points along the bed. The fourth measurement port is located at the throat section. The assumption is that if the third-point temperature is lower than the second one, the complete decomposition occurs at the mid-section of the bed and the gas just cools down after this point. It means that the chamber might be shortened in order to reach maximum temperature at the outlet.

Successful performance of the first phase of the test campaign results in selection of the most promising candidates for the next stage of research. It is assumed that during the second phase catalysts will be tested using a new chamber. The length of a new catalyst bed will depend on results (temperature profiles of each thermocouple) of the first part. The final stage will be based on configuring and testing of composite beds, consisting of finally selected catalysts.

Considering a small scale of the in-house production of 98 %+ HTP, which is probably not available anywhere else in Europe, its quantity was eventually limited to 320 cm^3 for a single experiment. Every test is divided into sub-sequences. Each sub-sequence consists of three short flows. The first sub-sequence, which is a cold start, contains 5, 3 and 2-second pulses with 5-second stops. After that, the chamber is cooled down to 200 °C and 2-second flows make the second sub-sequence. The third one in initiated after the average temperature of the catalyst bed is 400 °C. Fourth and fifth sub-sequence is possible depending on chamber conditions. The test is run until the propellant tank is emptied. The test sequence is presented in Tab. 1.

Tab. 1. Test sequence for the first stage of the test campaign [Author, 2014]

Sub-sequence	**Start**	**Flow s**	**Pause s**	**Flow s**	**Pause s**	**Flow s**	**Σ s**
I	Cold	5	5	3	5	2	10
II	200 °C	2	2	2	2	2	6
III	400 °C	1	1	1	1	1	3
IV, V, ...	*Hot*	*1*	*1*	*1*	*1*	*1*	*3*

Each part of the test is controlled by the computer, including solenoid valves opening and data acquisition. Some parameters are continuously monitored, such as: tank pressure and temperature, catalyst bed temperature.

Photographs presented in Fig. 6 show selected video frames from the first sub-subsequence of the selected test – a cold start. T_0 is the moment, at which the main valve starts to open. After 0.2 s some outflow occurs. It is visible up to about 1 s. After 1 s it can be barely observed. In case of a hot start the outflow is continuously invisible.

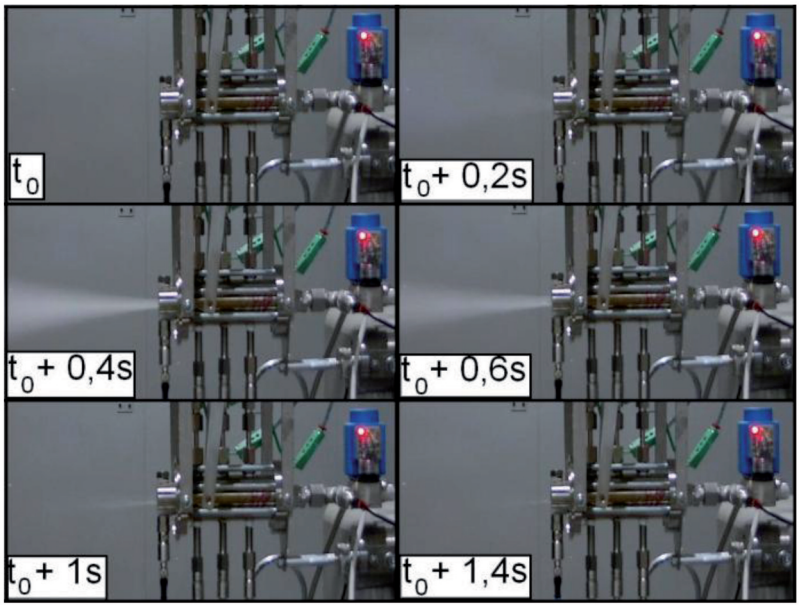

Fig. 6. Video frame sequence of a single test (hot start) [13]

5. TEST RESULTS AND ANALYSIS

The first phase of research (consisting of 50 tests) delivered almost 200 plots of parameters. Fig. 7 and Fig. 8 present results of the first and the second sub-sequence of a test of 4.8 mm α-alumina spheres, with low surface area and 11.5 % of active phase. Interesting is especially the cold start (Fig. 7). Temperature at the first cross section does not exceed 220 °C for the whole flow time. The second thermocouple indicates the same temperature for 3 s and then rapidly increases. In fact, 220 °C is the boiling point of 98 % hydrogen peroxide at 8 bar (current chamber pressure). The portion of decomposed HTP produces the amount of heat which heats up the remaining, not decomposed medium to its boiling point. The longer distance from the injector plate the more heat is generated by the process of decomposition. The third measurement point indicates the cross section in which the boiling point is not a barrier – the temperature builds up smoothly and instantly, reaching 700 °C after 5 s of flow.

After the propellant valve is closed, the backflow heat transfer occurs. A sudden temperature rise up to 600 °C may be noticed is the first section of the catalyst bed. When the propellant valve is opened for the second and the third time, the temperature at this section rises even more. It means that activity of a catalyst changes with initial temperature.

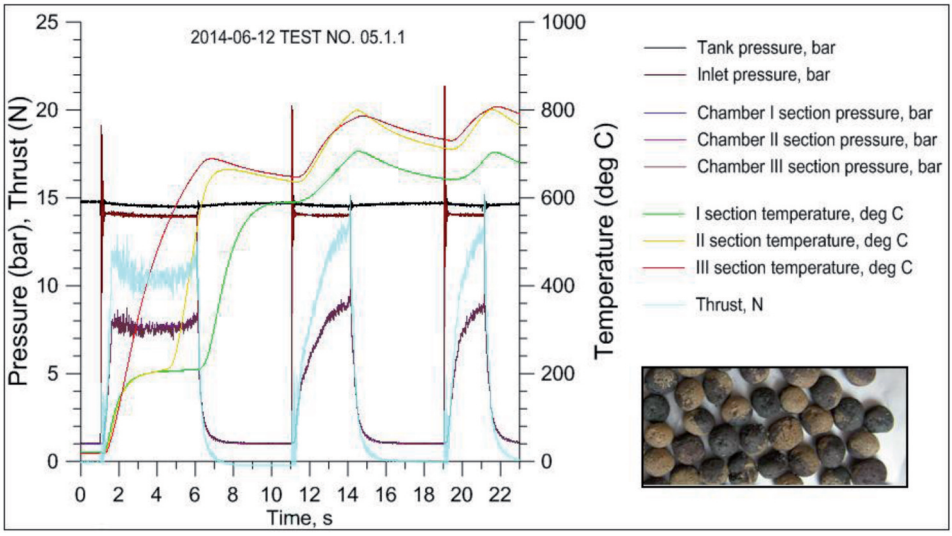

Fig. 7. Test result: 4.8 mm α-alumina spheres, low surface area, 11.5 % of active phase, cold start [Author, 2014]

When started from 200 °C, the situation is similar (Fig. 8). The first thermocouple indicates a slight increase of temperature, to 220 °C. The second-point temperature increases slowly for 1 s and then rapidly builds up, reaching 560 °C. Maximum temperature is lower than in the previous case (Fig. 7) because of the shorter flow time. Furthermore, relatively low temperature of decomposition products makes the chamber pressure lower than the design value. Since the maximum temperature reached in this case (800 °C) is much below the theoretical, it indicates relatively low quality of decomposition.

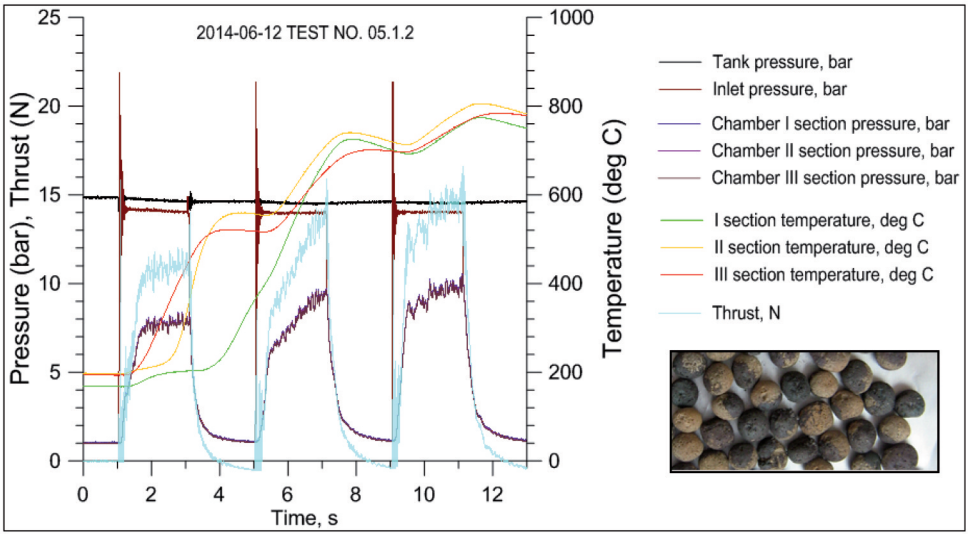

Fig. 8. Test result: 4.8 mm α-alumina spheres, low surface area, 11.5 % of active phase, 200 °C start [Author, 2014]

Plots presented in Fig. 9 and Fig. 10 show results of bi-modal γ-alumina 3.2 mm pellet support with high surface area (250 m^2/g) and 6.5 % of active phase. Both temperature build-up rate and maximum temperature are higher, comparing to the results presented in Fig. 7-8. In the first cross section the same phenomena as in the previous case can be observed. The temperature measurement unit indicates 230 °C, which is the boiling point of 98 % HTP at 10 bar (current chamber pressure). Temperature at both the second and the third cross section builds up quickly. The highest temperature for this sub-sequence (920 °C) is indicated at the second point.

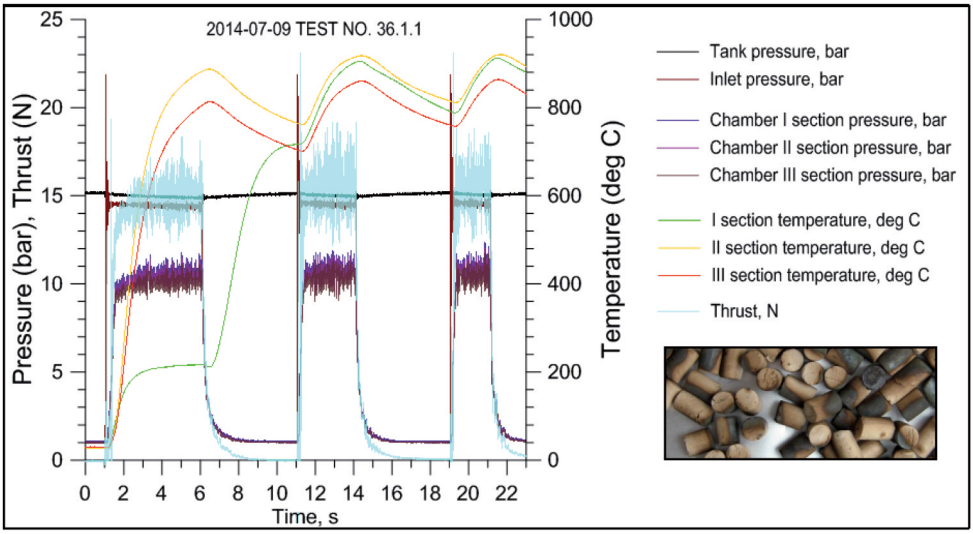

Fig. 9. Test result: 3.2 mm bi-modal γ-alumina pellets, high surface area, 6.5 % of active phase, cold start [Author, 2014]

Maximum temperature that was measured during this test was 940 °C – it almost covers the theoretical temperature of adiabatic decomposition of 98 % hydrogen peroxide. Chamber pressure was consistent with the design. Pressure drop between the first and the third cross section equals 0.5 bar (it is 5 % of the nominal chamber pressure). The estimated overall catalyst bed pressure drop (between the injector and the aft support plate) is 1 bar.

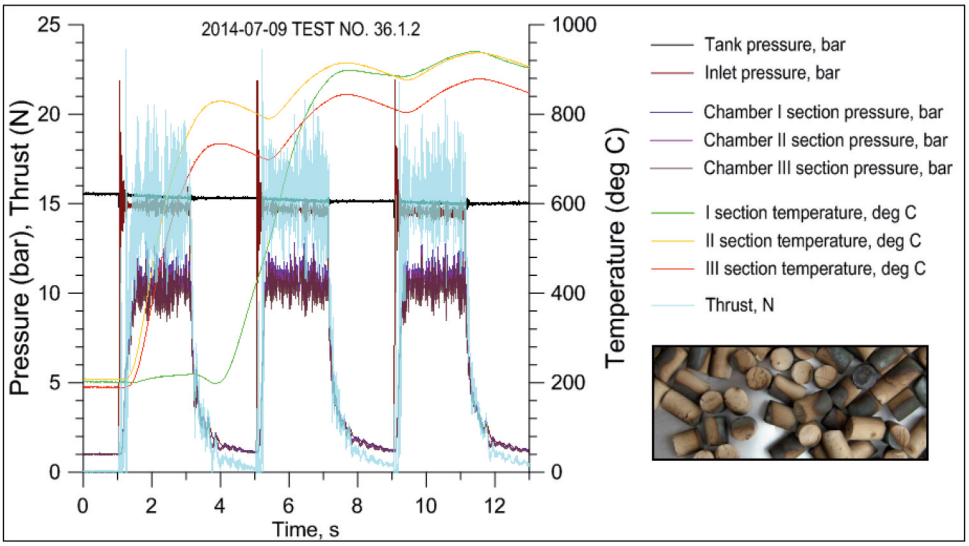

Fig. 10. result: 3.2 mm bi-modal γ-alumina pellets, high surface area, 6.5 % of active phase, 200 °C start [Author, 2014]

Fig. 11 presents the summery of the first stage of research in the form of the plot of maximum temperature for the first sub-sequence, first flow (5 second, cold start), obtained for all tests of catalyst samples. The best performance of a catalyst bed is reached with high surface area pellets, regardless the active phase content. Lowest values are for low surface area spheres, including zeolites. Moreover, both zeolites and tri-modal rings are prone to cracking.

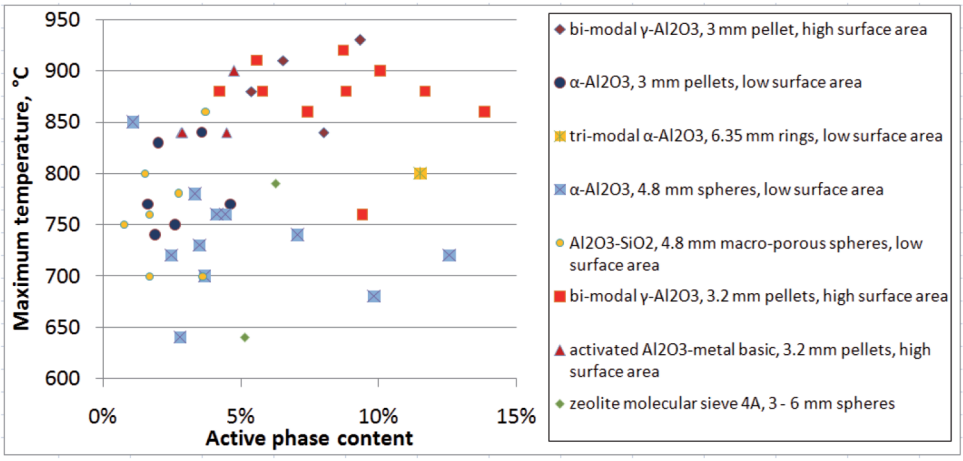

Fig. 11. Maximum temperature obtained after five-second HTP flow (cold start) for various tests and types of support [Author, 2014]

6. CONCLUSIONS

The experimental evaluation of 98 % hydrogen peroxide decomposition on various types of Al_2O_3/Mn_xO_y catalysts have been described in the paper. The aim of this part of research was to select the most promising candidates among all types of ceramic support tested in the framework of the current project. Selected candidates will be further investigated during the second phase of the test campaign.

The detail analysis of results proved that in most cases the highest temperature is indicated at the second measurement port, that is 50 mm from the injector plate. As a result, for further testing of selected catalysts a new 50 mm casing will be used. From among 50 samples, tested in the first stage of research, 10 catalysts have been selected for the second phase. These are mainly high surface area γ-alumina pellets as they give better performance than catalysts based on low surface α-alumina. Additionally, one sample of silica-stabilized macro-porous spheres have been chosen since it has the potential to be applied in a composite catalyst bed.

Summarizing the current research, ceramic alumina support impregnated with manganese oxides seem to be very attractive solution for decomposition of 98 %+ HTP. The current investigation shows that these catalyst are efficient and low-cost. Very important thing is the right selection of support, because performance of a catalyst bed strongly depends on this factor.

Technology readiness level for this stage of development is TRL3. Further work will contain the catalyst lifetime investigation and environmental research. This kind of catalyst bed might be applied to monopropellant and bipropellant thrusters as well as larger liquid and hybrid engines for upper stages of launch vehicles. Presented research seems to be original because of the use of the highest grade of HTP and the configuration of a catalyst bed which is close to the real operation conditions of rocket propulsion.

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REFERENCES

[1] ASD-EUROSPACE. (2012). Exemption of Propellant-related Use of Hydrazine from REACH Authorization Requirement.
[2] Bramanti, C., et. al. (2006), Experimental Characterization of Advanced Materials for the Catalytic Decomposition of Hydrogen Peroxide, 42nd AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit, Sacramento, CA.
[3] Do, S., Batchelor, B., Lee, H. (2009). Hydrogen Peroxide Decomposition on Manganese Oxide (Pyrolusite): Kinetics, Intermediates and Mechanism, Chemosphere, Vol. 75, p. 8-12.
[4] Dyer, J., Dinardi, A., Anflo, K. (2013). First Implementation of High Performance Green Propulsion in a Constellation of Small Satellites, 27th Annual AIAA/USU Conference on Small Satellites. Logan, UT, USA.
[5] European Chemicals Agency. (2011). Agreement of the Member State Committee on the Identification of Hydrazine as a Substance of Very High Concern.
[6] Evonik Industries AG. (2014). About hydrogen peroxide – Grades. [Online], http://h2o2.evonik.com/product/h2o2/en/about/grades/pages/default.aspx.
[7] Gordon, S., McBride, B. (1994). Chemical Equilibrium with Applications, NASA Glenn Research Center, Cleveland.
[8] Hasan, M., Zaki, M., Pasupulety, L. (1999). Promotion of the Hydrogen Peroxide Decomposition Activity of Manganese Oxide Catalysts, Applied Catalysis A: General, Vol. 181, p. 171-179.
[9] Kappenstein, C., Pirault-Roy, L., Guerin, M., Wahdan, T., Ali, A., Al-Sagheer, F., Zaki, M. (2002). Monopropellant Decomposition Catalysts V. Thermal Decomposition and Reduction of

Permanganates as Models for the Preparation of Supported MnOx catalysts, Applied Catalysis A: General, Vol. 234, p. 145-153.
[10] Loroch, L., Rams, L. (2014). Research Infrastructure and Organization Structure of Center of Space Technologies in the Institute of Aviation (in Polish), *Transactions of the Institute of Aviation*, *No. 1*(234), Warsaw, pp. 17-24.
[11] Micoli, L., Bagnasco, G., Turco, M., Trifuoggi, M., Russo Sorge, A., Fanelli, E., Pernice, P., Aronne, A. (2013). Vapour Phase H2O2 Decomposition on Mn Based Monolithic Catalysts Synthesized by Innovative Procedures, Applied Catalysis B: Environmental, p. 516-522.
[12] Military Specifications. (2003). Performance Specification; Propellant: Hydrogen Peroxide, MIL-PRF-16005F Rev. F.
[13] Rarata, G., Surmacz, P. (2014). Developing and Testing New Composite Catalyti Bed for Decomposition of 98 % HTP, 2014, 65th International Astronautical Congress, Toronto, Canada.
[14] Spores, R., Masse, R., Kimbrel, S., McLean, C. (2013). GPIM AF-M315E Propulsion System, 49th AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit, San Jose, CA.
[15] Swedish Defence Research Agency. (2010). GRASP Workshop.
[16] Surmacz, P., Rarata, G., Sobczak, K., Wolański, P. (2013). Investigation of a Labscale Hybrid Rocket Engine, VIII International Scientific Conference: Development Trends in Space Propulsion Systems, Warsaw.
[17] Surmacz, P., Rarata, G. (2014). Research on Catalytic Decomposition of Hydrogen Peroxide Using Al_2O_3/Mn_xO_y Catalysts Promoted by Transition Metal Oxides (in Polish), *Transactions of the Institute of Aviation*, *No. 1*(234), Warsaw, pp. 51-61.
[18] Winter, M. (2014). Silver physical properties. [Online], http://www.webelements.com/silver/physics.html.
[19] Wiśniowski, W., Wolański, P. (2014). Institute of Aviation Activities in the Field of Space Research (in Polish), *Transactions of the Institute of Aviation*, *No. 1*(234), Warsaw, pp. 9-16.

WPŁYW RÓŻNYCH RODZAJÓW KATALIZATORÓW AL_2O_3/MN_XO_Y NA OSIĄGI ZŁOŻA KATALITYCZNEGO O DŁUGOŚCI 100 MM W ROZKŁADZIE 98 % NADTLENKU WODORU

Streszczenie

Artykuł prezentuje wyniki badań katalitycznego rozkładu nadtlenku wodoru o stężeniu 98 % przy zastosowaniu specjalnych struktur, zwanych kompozytowymi złożami katalitycznymi. Takie konfiguracje złóż mogą znaleźć zastosowanie w przyszłości w rakietowych silnikach korekcyjnych systemów kontroli położenia (sztucznych satelitów) oraz w silnikach rakietowych na dwuskładnikowy ciekły materiał pędny o samoczynnym zapłonie i zdolności do ponownego uruchomienia.

W celu przeprowadzenia kompleksowych badań rozkładu 98 % nadtlenku wodoru przygotowano znaczną liczbę próbek katalizatora, z nośnikiem w postaci tlenku glinu oraz z tlenkami manganu w roli fazy aktywnej. Celem bieżącej fazy badań jest wybranie najbardziej obiecujących kandydatów do dalszych prac badawczych, przy użyciu komory katalitycznej o długości 50 mm. Wybór ten jest podyktowany wynikami dotychczasowych badań, w których wzięto pod uwagę dynamikę procesu rozkładu. Innym kryterium wybory jest integralność strukturalna złoża katalitycznego, oceniana po przeprowadzeniu każdego doświadczenia. Nośniki, będące podanymi na pękanie, nie mogą zostać zakwalifikowane jako odpowiednie do badania w kolejnej fazie.

Wyniki dotychczas przeprowadzonych badań dowodzą, że krytycznym czynnikiem determinującym osiągi katalizatora jest jednostkowe pole powierzchni nośnika. Najwyższe tempo wzrostu ciśnienia i temperatury wewnątrz złoża zanotowano dla mikroporowatych granulek γ-Al_2O_3.

Słowa kluczowe: napęd kosmiczny, nadtlenek wodoru, rozkład katalityczny.