Preliminary studies on self-sustained high-temperature synthesis of magnesium compounds

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Abstract
Self-sustained High-temperature Synthesis (SHS) is an innovative way to produce nowadays about 500 compounds and it is appliable to a wide class of reactions in condensed matter which yields solid products. Starting from a vast knowledge on solid/gas reactions (obtained studying solid rocket propellant and graphite combustion), solid/solid degradation (studies on thermal protection for space applications) and experiences with related diagnostics, preliminary studies on SHS have been carried out using $C0_2$ laser as reaction initiator and μ thermocouples as diagnostics. Formation of Mg compounds by SHS has already been reported in literature and further applications are here suggested.

Riassunto
Il processo di sintesi ad alta temperatura autosostenuta (SHS) è un metodo innovativo impiegato attualmente per la produzione di circa 500 composti e puo essere applicato ad una vasta gamma di reazioni solido/solido. Una ampia pregressa esperienza nei campi delle reazioni solido/gas (ottenuta lavorando sulla combustione di propellenti solidi per razzi e grafite) ha permesso di acquisire competenze non solo sul processo, ma anche sulle relative diagnostiche. Negli studi preliminari qui descritti e utilizzato un laser a $C0_2$ come iniziatore del processo SHS e μ termocoppie come diagnostica. La formazione di composti a base di Mg è già riportata in letteratura ed alcune originali applicazioni sono qui suggerite.

INTRODUCTION

Self-sustained High-temperature Synthesis (SHS) already stepped forward from a scientific discovery to a process whose field of application is wide (ref. 1). Many intermetallic compounds, ceramics, advanced alloys and composite materials can today be produced by SHS. The basic principles, ref. 2, controlling the solid flame are well known and borrowed from the studies carried on during many years on solid/gas reactions. SHS as, for instance, solid rocket propellant combustion needs external energy supply to initiate the process and an exothermic reaction to sustain the combustion. In both cases the existence of a moving process surface allows to model a two phase system: solid/gas for solid propellant and solid/solid for SHS products. Fig. 1 shows the experimental set up available at TEMPE-C.N.R. for solid propellant driven combustion studies (ref. 3). A $C0_2$ laser (λ= 10.6 μm, P= 75 W, TEM_{00}) is used for ignition, extinction and, modulating its emission, response function studies. By the help of this supplier of precisely controlled external energy, ignition transients, stability boundaries and response frequencies have been determined for a remarkable variety of solid propellant at various operating conditions. For what is related to thermal aspects quite easily transferable to SHS studies, Fig. 2a depicts the ignition process of a solid propellant. A 25 μm Pt/Pt-Rh thermocouples, placed on the irradiated propellant surface, follows the heating up of a solid propellant (caused by the infrared laser beam impinging on the surface) and the ignition while, marked by the abrupt raise of the surface temperature, is well defined. At this very moment combustion gases (whose velocity is measured by a Laser Doppler Velocimeter, ref. 4) start flowing out as presented in Fig. 2b. These experiments allow to measure ignition delay time, ignition temperature, ignition energy (ref. 5) and from these data macrokinetics characteristics can be computed (ref. 6).

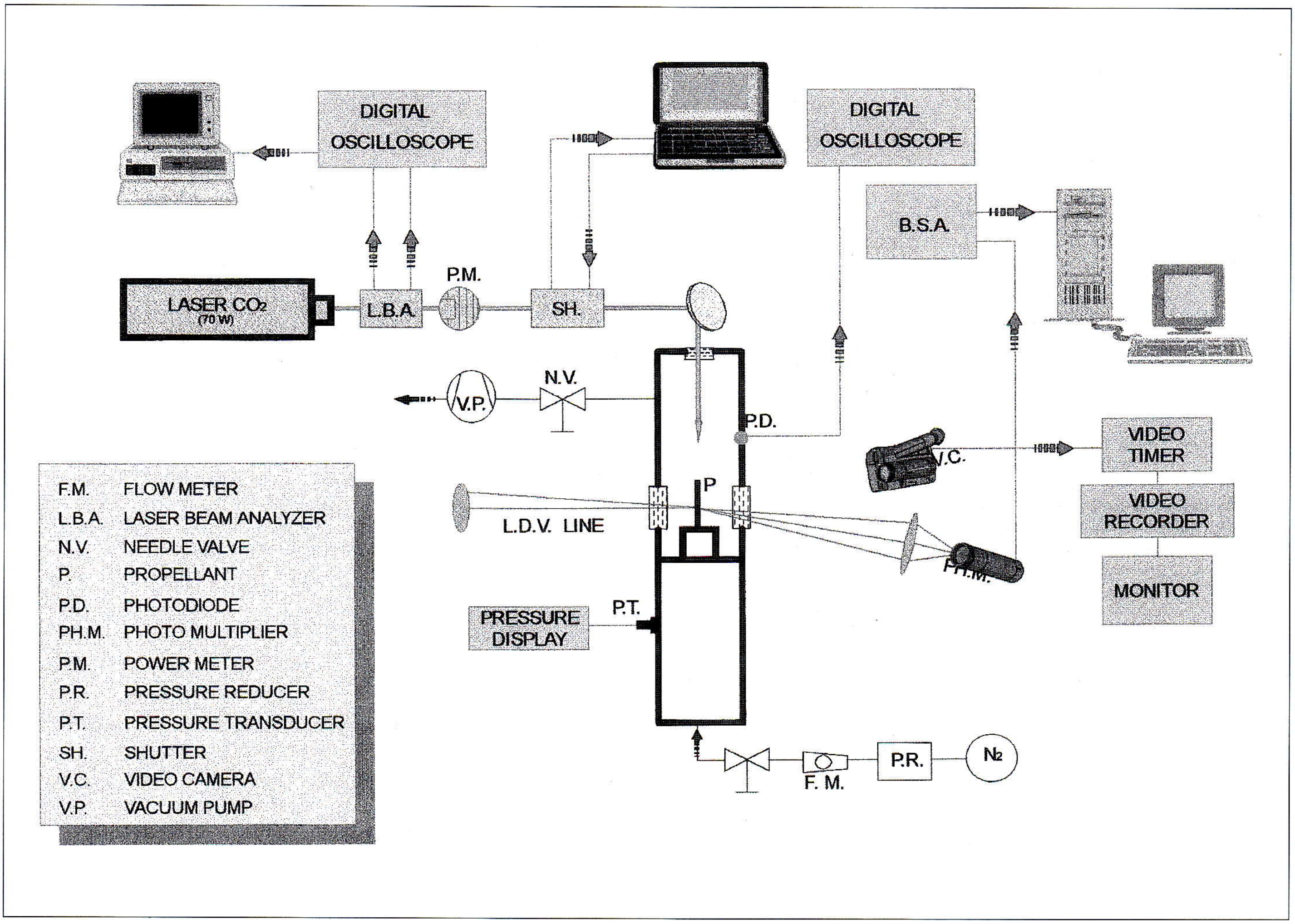

Figure 1: Experimental setup

EXPERIMENTAL RESULTS

All the tests here reported are carried out at constant subatmospheric pressure keeping an Ar flow in the combustion chamber. The vertical axis of the chamber (Fig. 1) is aligned with the laser beam and, along its path, an electromechanical shutter, a power meter and a laser beam analyser are placed. To enhance the radiation stability (in terms of power and Gaussian profile) the laser is operating in CW mode and its target can be adjusted on its support in order to guarantee the best alignment. During these ignition studies, sharp and fast raising of the incident radiation is obtained by operating the high speed shutter (controlled by a PC) with an opening time, $t_o = 20$ μs. By this experimental apparatus, preliminary SHS tests have been conducted igniting samples of pressed powders by one $C0_2$ laser pulse of suitable duration. Referring to previous experiments with rocket propellants the SHS experimental requirements looked less critical due to the longer ignition delay time involved in this process. Fig. 3 shows the NiAl (70/30 by weight) heating and ignition process detected by a 50 μm μthermocouple when the laser is impinging on the surface with beam diameter ϕ_b= 4 mm and total power P= 65 W. The heating up of the sample depends on the mixture characteristics and suggestions concerning exothermic reactions are revealed at temperature ≈640°C which is close to that of the Al melting point. The actual beginning of a reactive process is pictured by the sharp increase of the thermocouple signal when the laser, after a pulse duration t_p= 404 ms, has already been turned off. Tests conducted on similar mixtures shown that SHS process takes place after reaching the Ni melting temperature (1728 K) with analogous behaviour of propellant combustion where the reaching of the ignition temperature is a necessary, but not sufficient conditions to give steady

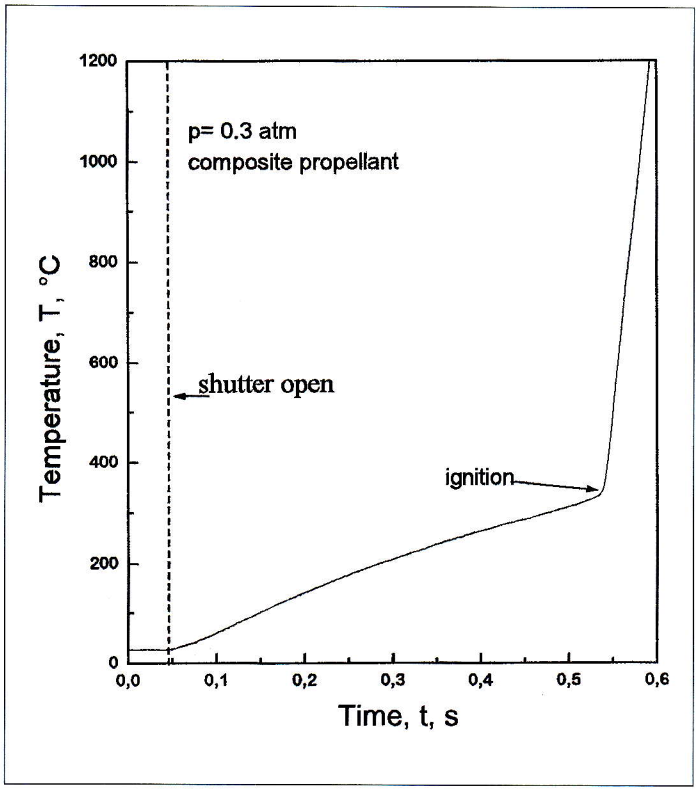

Figure 2a: Temperature history during the heating and ignition processes

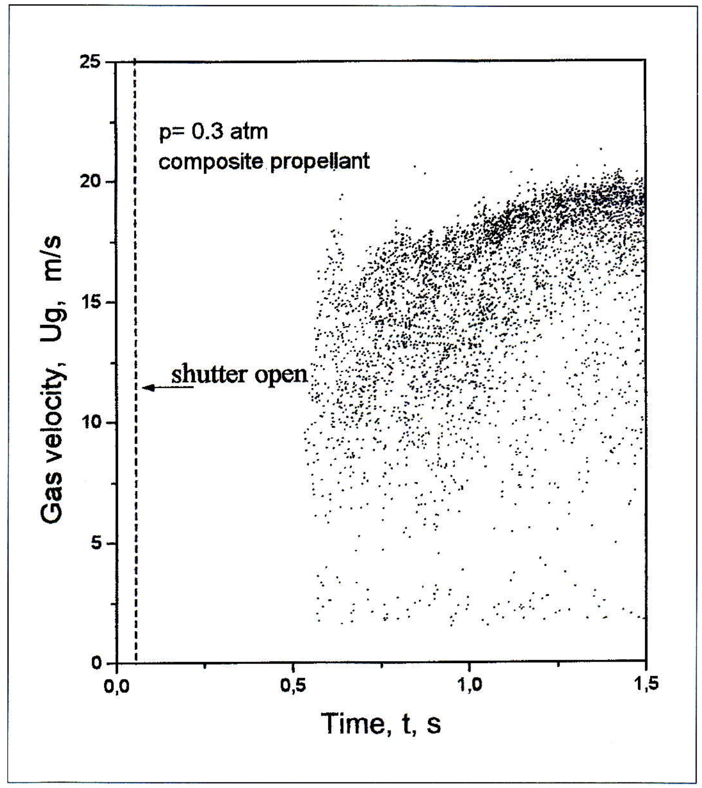

Figure 2b: Gas velocity history during the heating and ignition processes

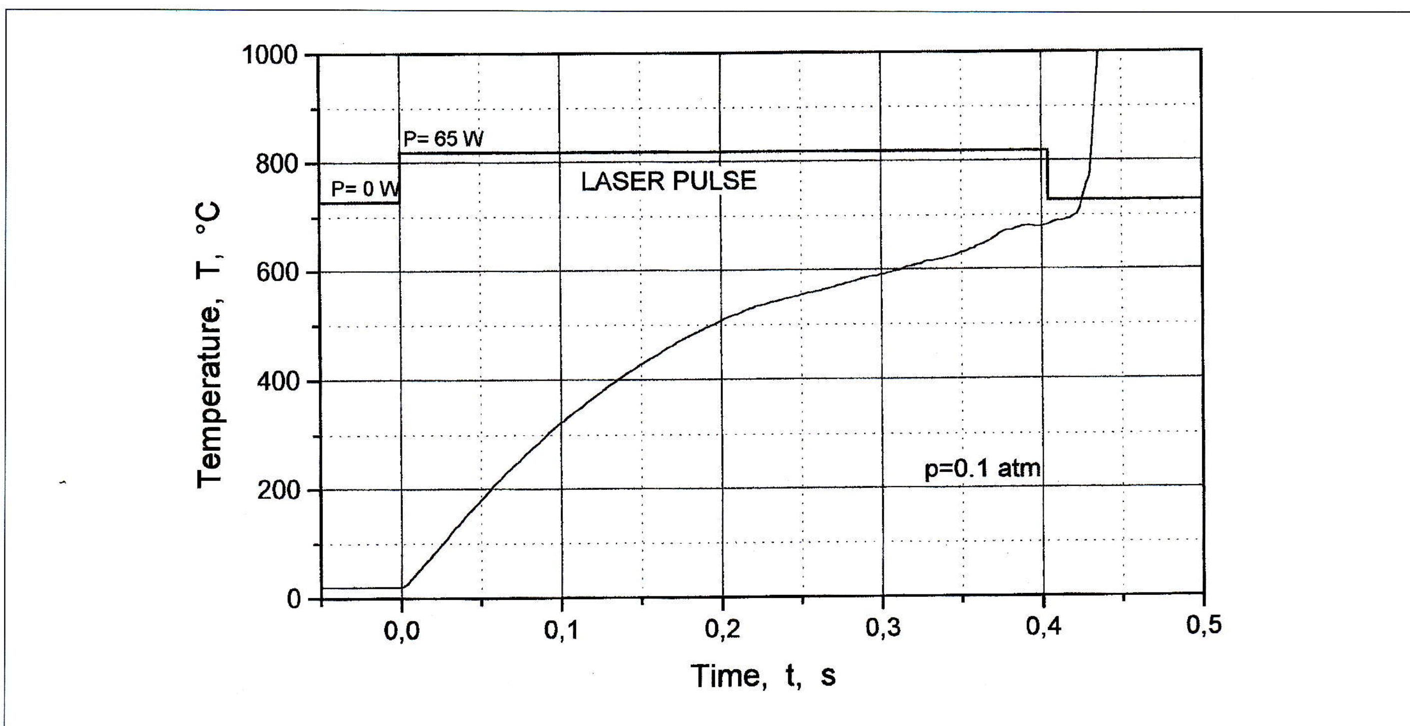

Figure 3: Temperature history of NiAl powder mixture following heating by CO_2 laser beam

burning. Fig. 4 shows SHS process with ZrBq (81/19 by weight)and in this case a different behaviour is displayed. Heating process of the sample shows more complex structure and, before the blown off of the thermocouple (1500°C), no self sustained reactions are activated. Furthers experiments will be carried on by W/Re thermocouples which allows higher working temperature (2800°C).

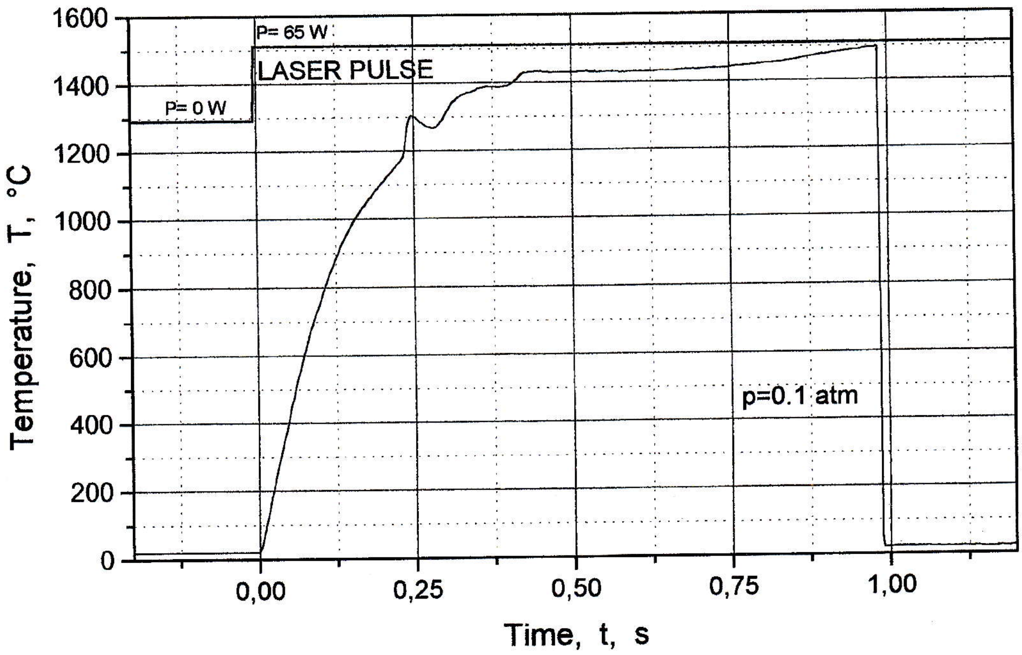

Figure 4: Temperature history of ZrB_2 powder mixture following heating by CO_2 laser beam

DISCUSSION

Analogous experiments, where however ignition has not be obtained by laser, have been carried out also on Mg compounds and in literature results have been already reported: Mg_3N_2 suitable for coatings, MgA1q0~ for thermal protections in furnaces, various Mg applications for pigment production, $CaW0_4$-Mg combustion studies for pure tungsten production, and many ceramics applications for filtering. Future tests with the described experimental apparatus will be focused on those mixtures where Al can be substitute by Mg. Mg_2Ni is a promising alloy for hydrogen storage and $MgNi_2$ which is an intermetallic compound with low adiabatic temperature. In this latter case $C0_2$ laser can supply external energy during the process in order to have a propagating thermal wave in the solid. Despite different energy supplier systems (generally based on electric field effect on transfer properties) has been already employed, $C0_2$ laser system looks even more promising.

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