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MAGNESIUM – AN IMPORTANT COMPONENT OF HIGH-ENERGY COMPOSITIONS

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Abstract

Magnesium is a widely used component in high-energy compositions. Mixtures containing this metal can be found in show and military pyrotechnics, rocket propellants and various explosive masses. Magnesium containing compositions have high combustion temperature, which allows one to achieve the desired special effect. Two important stages in designing new high-energy mixtures, i.e. compatibility of substances and optimal composition, were described. The calculations were based on mixtures containing magnesium. In line with the standard STANAG 4147, using differential scanning calorimetry, compatibilities of mixtures of magnesium with octogen (HMX) and magnesium with hekzaazahekzanitroizowurzitane (CL-20) were examined. Magnesium is compatible with these nitroamines. An optimal composition which ensures the maximum combustion temperature and specific impulse was determined using the calculation programme isp2001. The optimum composition of the Mg : HMX composition burns at a lower temperature than the Mg : CL-20 mixture. The combustion temperature was 3493K for the former mixture and 3807K for the latter one. The specific impulse determined for both compositions was 273s. The specific impulse was established for mixtures with different shares of magnesium. The mixture containing in octogen reached the maximum specific impulse at 5% Mg, while the mixture containing CL-20 reached the highest specific impulse at 15% of this metal.

The dependence of the specific impulse of rocket propellant containing polybutadiene with terminal hydroxyl groups (HTPB), ammonium perchlorate and magnesium was examined. The maximum value of the impulse increases with a decreasing amount of the binder. When another binder such as for poly(glycidyl azide) (GAP) was used, a reverse relationship was observed. The specific impulse increased with an increased binder content.

The influence of various oxidants on the combustion temperature of pyrotechnic mixtures was defined. The highest combustion temperature was achieved for compositions with the magnesium content in the range of 20 to 45%. The effect on combustion temperature of the oxidants polytetrafluoroethylene, potassium chlorate and iron oxide was compared.

Keywords: magnesium, application, combustion, calculations, pyrotechnics.

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MAGNEZ – ISTOTNY SKŁADNIK MIESZANIN WYSOKOENERGETYCZNYCH

Abstrakt

Magnez jest szeroko stosowanym składnikiem w mieszaninach wysokoenergetycznych. Układy zawierające ten metal znaleźć można w pirotechnice widowiskowej i wojskowej, w paliwach rakietowych oraz licznych mieszaninach wybuchowych. Mieszaniny zawierające magnez mają wysoką temperaturę palenia, co umożliwia osiągnięcie żądanego efektu specjalnego. Na przykładzie mas zawierających magnez przedstawiono dwa istotne etapy występujące podczas opracowywania nowych mieszanin wysokoenergetycznych, takie jak oznaczenie kompatybilności składników i określanie optymalnego składu mieszaniny. Zgodnie z normą STANAG 4147, z wykorzystaniem różnicowej kalorymetrii skaningowej zbadano kompatybilność magnezu z oktogenem (HMX) i z heksaazaheksanitroizowurcytanem (CL-20). Magnez jest kompatybilny z tymi nitroaminami. Wykorzystując program ISP2001, wyznaczono optymalny skład mieszanin umożliwiający osiągnięcie maksymalnej temperatury palenia lub impulsu właściwego. Mieszanina Mg : HMX o optymalnym składzie spala się w niższej temperaturze niż mieszanina Mg : CL-20. W przypadku pierwszej z wymienionych mieszanin temperatura spalania to 3493K, natomiast drugiej 3807K. Wyznaczony dla obydwu mieszanin impuls właściwy osiągnął tę samą wartość równą 273s, przy różnej zawartości magnezu. Mieszanina zawierająca w swoim składzie oktogen maksymalną wartość impulsu osiągnęła w przypadku 5% zawartości Mg, natomiast zawierająca CL-20 – 15% zawartości metalu.

Zbadano zależność impulsu właściwego od składu paliwa rakietowego zawierającego polibutadien z końcowymi grupami hydroksylowymi (HTPB), chloran (VII) amonu i magnez. Maksymalna wartość impulsu zwiększa się wraz ze zmniejszeniem zawartości lepiszcza. Po zmianie lepiszcza na poliazydek glicydylu (GAP) zaobserwowano odwrotną zależność. Maksymalny impuls właściwy wzrastał, gdy rosła zawartość lepiszcza w paliwie.

Określono wpływ różnych utleniaczy na temperaturę palenia mieszanin pirotechnicznych. Najwyższe temperatury spalania uzyskano w przypadku mieszanin o zawartości magnezu od 20 do 45%. Porównywano wpływ na temperaturę spalania następujących utleniaczy: politetrafluoroetylenu, chloranu(VII) potasu oraz tlenku żelaza.

Słowa kluczowe: magnez, zastosowanie, spalanie, obliczenia, pirotechnika.

INTRODUCTION

Magnesium is an essential miroelement for live organisms for a number of reasons. Above all, it participates in many metabolic processes. Besides, it is found in the cellular nucleus, whose functions it sustains. Moreover, owing to its high biochemical activity, magnesium is a valuable metallic co-enzyme in over 300 reactions of phosphate transfer (BAKER 2002, PASTERNAK et al. 2010). Magnesium is also an important ingredient of high-energy mixtures containing an oxidant and a reductant. An oxidant contained in mixture facilitates its combustion without access to air oxygen, which means that the desired special effect is possible. Magnesium containing compositions have found a broad range of applications in show and military pyrotechnics, in rocket propellants and explosive mixtures. The MTV compositions, made of magnesium, polytetrafluoroethylene (PTEE) and Viton, are popular in military pyrotechnics. While burning these mixtures reach high temperature and generate solid reaction products. Thus, they can be successfully used in igniter systems to blow up powder loads (Gocmez 1999). The intensity of infrared radiation in a narrow range of wavelengths means that MTV compositions can be used in decoy flares and in thermal traps. MTV compositions are also used in tracers, where they make a projectile trajectory visible (Koch 2002). It is possible to achieve more intensive emission of infrared radiation by replacing PTEE with carbon polyflouride – CF_x (Koch 2005). CF_x reacts with magnesium and other metals in a highly exothermic autocatalytic reaction (Cudziło et al. 2007). Compositions of magnesium with PTEE and Viton present several valuable characteristics, such as low hygroscopicity, easy processing (pelleting, pressing), weak dependence of combustion rate on pressure or temperature, and burning stability at low pressure and temperature. Besides, these mixtures are safe while making and storing (Boskovic, Negoicic 2009). In military pyrotechnics, magnesium containing compositions are used, for example, in red (Zagidullinovich 2012) and orange (Korobkov et al. 2010) flare masses, in firecrackers (Yueming 2003) and in Bengal fireworks (Lyadov, Kuznetsov 1997).

In order to improve the stability of pyrotechnic compositions, magnesium and aluminium alloys are often used (Lyadov, Kuznetsov 1997, Yueming 2003, Zagidullinovich et al. 2012), e.g. composed of 54% of magnesium by weight. Such alloy is an intermetallic compound Al_3Mg_4, which – compared to magnesium - is less reactive and more fragile, which makes it is easier to be ground (Szydłowska 1957). Another method which enhances the stability of magnesium is the modification of its surface (Smith 2009).

Magnesium is used in solid heterogeneous rocket propellants, especially in amateur applications (http://rakiety.pomorze.pl/Stronadomowa/atakna10km.htm, http://www.nakka-rocketry.net/propel.html). In some situations, the presence of magnesium in fuel is undesirable because while burning it will emit large amounts of combustion products. To eliminate the trail following a rocket, metals and ammonium perchlorate (AP) should be replaced with other substances (Książczak et al. 2005). The metal is substituted by high-energy compounds, such as hexogen (Flanagan 1994), whereas AP is replaced with ecological oxidants, e.g. ammonium dinitroamide (Gołofit et al. 2013).

The purpose of this study, carried out on two compositions with magnesium, has been to demonstrate two essential stages which must be proceeded through while designing new high-energy compositions: determination of the compatibility of components and an optimal composition of a new mixture.

DISCUSSION

The first step when elaborating new, effective and stable high-energy compositions is to analyze the compatibility of components. Compatibility is achieved when there is no negative influence of one mixture component on the chemical stability of the other component. The norm regulating compatibility investigations is the STANAG 4147 (NATO STANAG 4147MMS 1992). One of the applicable methods is the comparison of the decomposition peak maximum temperature (T_{max}) of individual substances and their mixtures, determined by differential scanning calorimetry (DSC) or differential thermic analysis (DTA). Non-compatible compositions are mixtures for which the T_{max} of decomposition is by 20K more than the T_{max} of the less stable component. If the said difference is within the range of 4 to 20 K, then the composition possesses an unsure compatibility. A mixture whose decomposition T_{max} is no less than 4 K below the T_{max} of the less stable component is said to be a compatible composition.

Investigations were performed to determine the compatibility of magnesium with such nitroamides as octogen (HMX) and hekzaazahekzanitroizowurzitane (CL-20). Such compositions can be used in thermobaric explosives (CUDZIŁO et al. 1996, CHAN et al. 2004). Multi-component products with magnesium and nitroamides can also be used as rocket propellants (http://www.starmolecule.com/faq/rocket-fuel/). DSC determinations were accomplished on samples of components weighing 1 mg each and their mixtures weighing 2 mg. Analyses were made in the range of temperatures from 430 to 600 K, at a temperature increase rate of 2K min^{-1}, in aluminium vessels fitted with a hole. Figure 1 shows results of DSC analyses for magnesium (solid line), octogen (broken line) and their 1 : 1 composition (dotted line).

As expected, in the above temperature range, no exothermic peak associated with the oxygenation of a sample was observed for magnesium samples. The maximum decomposition peak appears at 554K for HMX, and at 556K for its mixture with magnesium. Hence, the two components are compatible. Also, the compatibility of magnesium with CL-20 was determined, with the results illustrated in Figure 2.

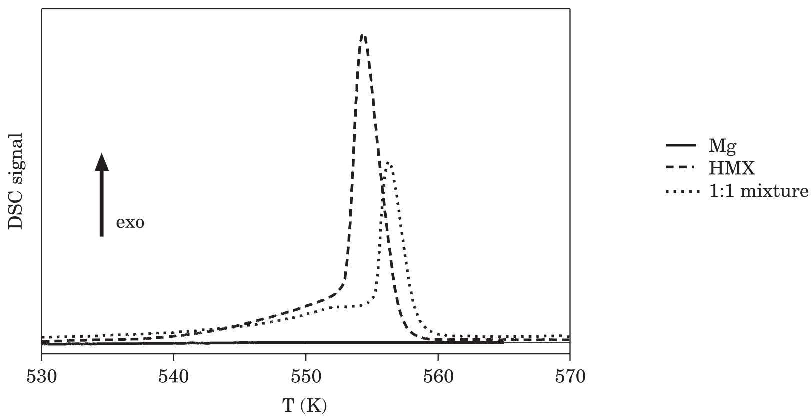

Fig. 1. DSC curves for decomposition of octogen, magnesium and their mixture in a 1:1 ratio by weight

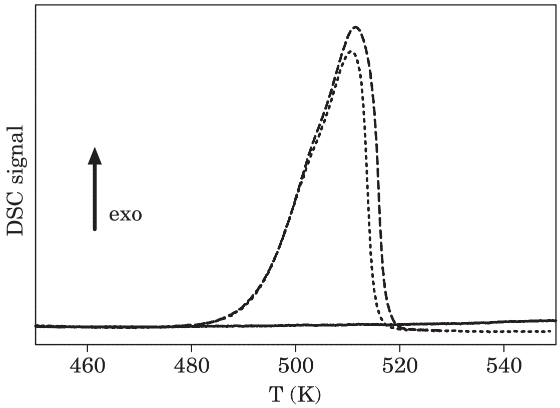

Fig. 2. DSC curves for decomposition of CL-20, magnesium and their mixture in a 1:1 ratio by weight

The maximum decomposition peak temperature for CL-20 was 511K, and for its composition with magnesium it decreased to 510K. Thus, magnesium was compatible with CL-20, same as it was with HMX.

Having determined the compatibility, it is then crucial to design such a composition of the mixture which would ensure the maximum special effect. For compositions used in decoy flares or in thermal traps, one of the significant parameters is the combustion temperature; in mixtures used as rocket fuel, it is their specific impulse (SINGH et al.1988), which characterizes the fuel efficiency. These two parameters were determined with the isp2001 software (http://www.dunnspace.com/isp.htm). For analyses on rocket propellant components, it was assumed that the pressure in the engine chamber was 70 atm and the gas expansion was up to 1 atm. Figure 3 depicts the effect of the magnesium content on specific impulse and combustion temperature in the analyzed compositions.

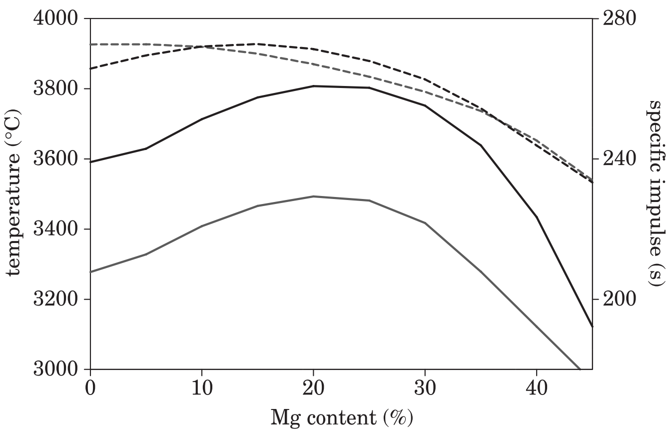

Fig. 3. Dependence of combustion temperature and specific impulse on the magnesium content in mixtures with octogen (HMX) and CL-20

In both cases, the highest combustion temperature was achieved for compositions containing about 25% of magnesium. The maximum combustion temperature was 3807K for the Mg and CL-20 mixture, and 3493K for the mixture of the same metal with HMX. The specific impulse of the magnesium and octogen composition was the highest (273s) at the 15% share of magnesium. The highest value of the specific impulse for compositions of magnesium with CL-20 was 273s, and it was obtained at a 5% contribution of Mg. Should we wish to achieve the highest combustion temperature, then the right composition is 25% Mg and 75% CL-20. In turn, if our aim is the maximum specific impulse, then the most appropriate mixtures are the ones composed of 5% Mg and 95% Cl-20 or 15% Mg and 85% HMX. Considering the costs of raw materials, the mixture with octogen is better. If it is more important to diminish the trail following a projected missile, then the composition with CL-20 is a better choice.

Heterogenic rocket fuels contain a binder . Below we discuss the results of our calculations for different compositions of fuel containing magnesium. The effect of magnesium on the specific impulse of fuel containing hydroxyl-terminated polybutadiene (HTBP), ammonium perchlorate and magnesium is illustrated in Figure 4.

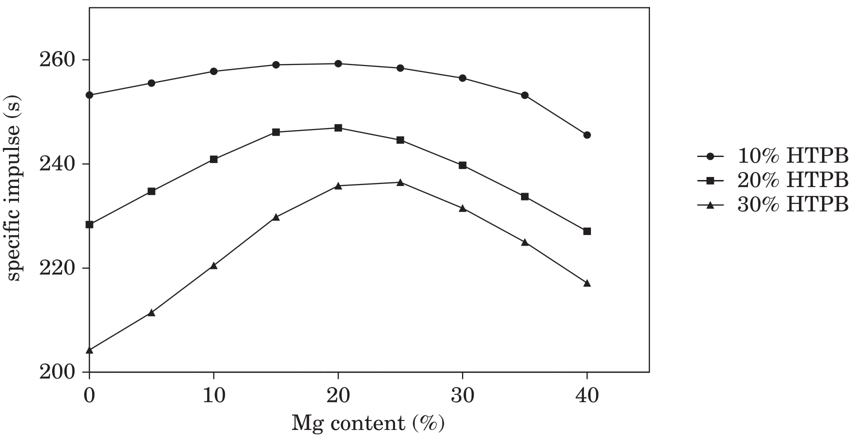

Fig. 4. Dependence of specific impulse on the composition of rocket propellant with HTPB, ammonium chlorate (VII) and magnesium

The specific impulse of a HTPB, AP and Mg composition containing 10% of the binder changes from 253s for the mixture without magnesium to 246s for the one with 40% of Mg, reaching the maximum of 259 s at 20% share of HTPB. For a composition containing 20% and 30% of the binder, the specific impulse changes from 228 and 204s in mixtures without magnesium to 227 and 217s, respectively, in compositions with 40% of magnesium up to the highest values of 245 and 236s in compositions with 20% and 25% of Mg, respectively. The specific impulse of compositions containing HTPB, AP and

Mg increases as the percentage of the binder decreases, and the maximum specific impulse at any tested share of HTBP can be noticed when the share of magnesium is 20 to 25%.

The influence of magnesium concentrations on the specific impulse of rocket fuel containing glycidyl azide polymer (GAP), ammonium perchlorate (AP) or magnesium is illustrated in Figure 5.

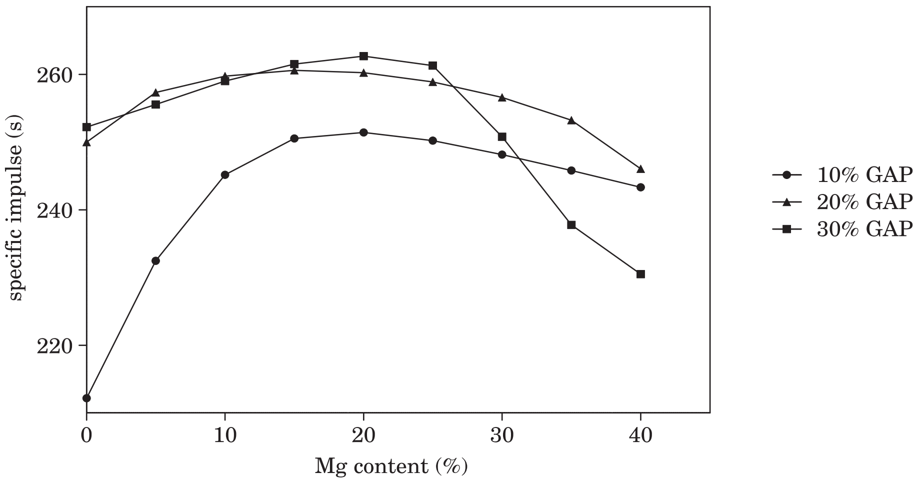

Fig. 5. Dependence of specific impulse on the composition of rocket propellants with GAP, ammonium chlorate (VII) and magnesium

The specific impulse of a composition of GAP, AP, Mg containing 10% of the binder changes from 212s in the mixture without magnesium to 243s in the mixture with 40% of Mg, reaching the maximum value of 251s at 20% share of GAP. For the composition containing 20 and 30% of the binder , the specific impulse changes respectively to 250 and 252s in mixtures without magnesium and 246 and 230s in mixtures containing 40% of Mg, reaching the highest values of 261 and 263s at 15 and 20% magnesium content, respectively. The specific impulse of compositions containing GAP, AP and Mg increases as the content of the binder increases, and at any given content of GAP, the maximum value of the specific impulse can be observed at the 15 to 20% share of magnesium.

Despite large differences in the properties of GAP and HTPB, similar values of the specific impulse were obtained for both agents, namely 263 for GAP and 259s for HTPB. The maximum values of the specific impulse for both polymers occurred at a similar content of magnesium.

Magnesium can also be used in pyrotechnic compositions used by the army and by civilians. In order to achieve the maximum special effect, it is extremely important to add appropriate amounts of magnesium to high-energy compositions. The effect of magnesium on the achieved pyrotechnic effect has been demonstrated based on calculations aided by a software programme package isp2001 [http://www.dunnspace.com/isp.htm].

The temperature of adiabatic combustion of the analyzed compositions used in the show and military pyrotechnics has been determined. This part of the study is worth underlining because we can observe the influence of oxygen on the value of combustion temperature (GRANSDEN, TAYLOR 2007). Figure 6 shows the dependence of the combustion temperature of pyrotechnic compositions on the content of magnesium. Calculations were made for mixtures containing from 5 to 50% magnesium by weight, assuming that the mixtures were burned at atmospheric pressure.

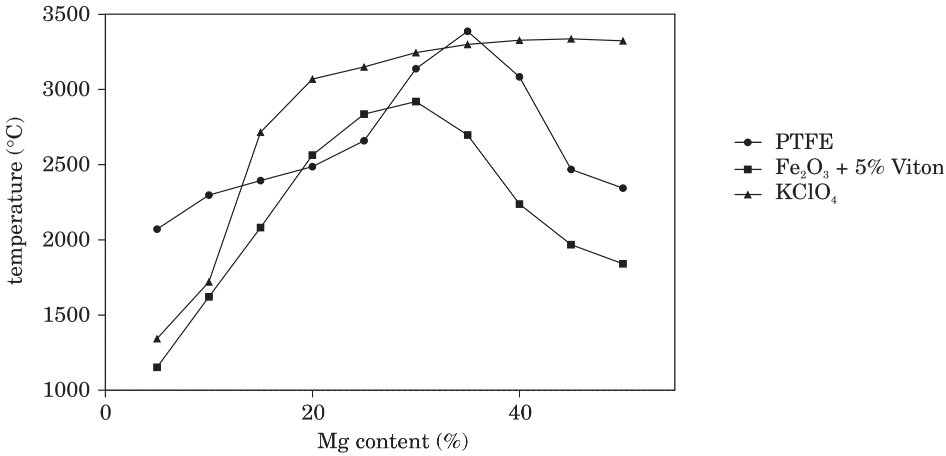

Fig. 6. Dependence of combustion temperature of pyrotechnic compositions containing polytetrafluoroethylene (PTFE), potassium chlorate (VII) or iron oxide as an oxidant with 5% Vitone

The combustion temperature of a mixture which contains politetrafluoroetylen (PTFE) and an oxidant changes from 2072K at the 5% magnesium content to 2344K at 50%, and reaches the maximum value at a 35% share of the reducer. These values coincide with literature data (DE YONG, SMIT 1991, KUWAHARA et al. 1997). The calculations for the compositions with iron oxide were carried out on the assumption that the fluoridated polymer Viton made up 5% of the whole content. The combustion temperature of such a mixture changes from 1153K at a 5% magnesium share to 1841K when magnesium constitutes 50% of the composition, reaching the maximum value of 2920K at a 30% share of the reducer. A composition of magnesium and potassium chlorate (VII) presents the combustion temperature of 1344K at a 5% share of the reductant to 3336K when the content of the metal is 45%. The combustion temperature of all mixtures increases when the content of magnesium increases, reaching its highest value at a 30 to 45% content of the metal. The combustion temperature of mixtures which contain polytetrafluoroethylene or iron oxide as an oxidant reaches the highest value within a low range of changes in the magnesium content. A composition of potassium chlorate (VIII) and magnesium has a high combustion temperature when the content of the oxidant varies from 20 to 50%.

SUMMARY

Magnesium is an essential component of high-energy compositions with civil and military applications. It is for example broadly used in show pyrotechnics, in thermobaric mixtures and in rocket propellants. Magnesium-containing mixtures have high combustion temperature, which enables the user to achieve the desired special effect. The actual effect depends on the percentage of magnesium in a composition. Thus, when designing new compositions, the early stages of work can be supported by calculation programmes, such as ISP2001 (http://www.dunnspace.com/isp.htm). Another aspect to keep in mind is the compatibility of components in a mixture. The determinations carried out in the current study prove that magnesium is compatible with HMX and CL-20. The calculations imply that it is possible to attain an approximately same specific impulse for both compositions, which would equal 273s. The maximum special effect is just one of the criteria taken to select components of new high-energy masses. Other criteria, e.g. price, safe application, simplicity of manufacture, trailing ability, stability, etc., help to select the most suitable ingredients for new high-energy compositions.

The specific impulse of rocket propellant containing polybutadiene with terminal hydroxyl groups (HTPB), ammonium perchlorate and magnesium increases as the content of a given binder decreases. When another binder, such as poly(glycidyl azide) (GAP) was used, a reverse dependence was observed. The maximum specific impulse increases as the amount of GAP increases. Through the comparison of combustion temperatures of the following oxidants: polytetrafluoroethylene, potassium chlorate (VII) and iron oxide, an optimum content of magnesium was set at 20 to 45%, depending on an oxidant.

Some limitation to the use of magnesium in high-energy compositions is due to its reactivity. This is the reason why it is often used in the form of an alloy with aluminium, such as Al_3Mg_4. Another solution is to modify the surface of magnesium.

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