Aluminium and zirconium powders as components of specialty pyrotechnics and rocket propellants

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Abstract: *Methods of obtaining aluminium and zirconium powders, decisively influencing their granulation and thickness of the passivation layer formed on the metal surface are discussed. Application of zirconium instead of aluminium can lead to ignition resulting from its high electrostatic discharge sensitivity. One of the ways to avoid this issue is to replace metallic zirconium with the* ZrH_2 *powder or to coat its surface with aluminium.*

Key words: *aluminium powder, zirconium powder, pyrotechnic, propellant*

1. Introduction

Powders of such metals as boron, aluminium, beryllium, magnesium and zirconium are made use of in specialty pyrotechnics and also as additives (the so called complementary fillers) in heterogeneous solid rocket propellant formulations [1]. One of the extensively used is powdered aluminium - 15 wt.%, with very fine (5 μm) and spherically shaped particles. Substituting it with zirconium powder or ZrH_2 makes it possible to increase propellant density from (1.5 - 1.8) g cm^{-3} to approximately (2.3 - 2.5) g cm^{-3}. Each of these complementary fillers causes increase of the propellant energy value and the rocket speed [2]. At the same time, ballistic efficiency is enhanced being almost by (35 – 45)% higher than when aluminium powder is used as the filler. Besides, application of powdered zirconium calls for considerably smaller amount of the excessive oxidizer in the propellant than using zirconium hydride.
The main issue regarding application of the above mentioned metal powders is their availability. In Poland, none of them is being manufactured. Therefore, their physicochemical characteristics related to the production method are of importance affecting the size of particles as well as thickness of the passivation oxide layer. Another issue is possibility to modify the phase composition of the surface of the available metal powders aiming at imparting to them some desired properties. Considering significant advantages resulting from replacing powdered aluminium with zirconium, the present study has been focused on methods of obtaining them and on the selected physicochemical properties.

2. Aluminium powder

Aluminium is manufactured by electrolysis while aluminium powder by application of several techniques determining its physicochemical properties. Among them there are such methods as:
- crushing of brittle aluminium alloys such as AL-Ni, Al-Mg or Al-Si in ball mills or other crushing devices;
- dry grinding of aluminium powder or foil in the presence of surfactants in an inert gas atmosphere with careful monitoring of the oxygen content in the atmosphere; this method is applied in order to obtain aluminium powder for production of pigments and in pyrotechnics [3];
- grinding of coarse grained aluminium particles suspended in a liquid phase (hydrocarbons or water) containing surfactants (SPC) or other additives which are necessary for obtaining pastes [3];
- granulation by introducing liquid aluminium into a cooling medium in order to obtain grains of the diameter (4 – 20) mm;
- centrifugal atomization consisting in directing a small stream of molten aluminium onto a rotating disc - the molten metal is being introduced into a cooling gas or water forming ball shaped particles; this method

permits to obtain aluminium powder with grain size (5 – 500) μm [4];
- hot crushing of big lumps of metal - the granules thus obtained feature irregular shape and grain size (5 – 20) mm;
- caking of thin foil to form ball shaped granules with diameters of (3 – 6) mm.

In Table 1, influence of the method adopted to prepare the aluminium oxide on alteration of some of its characteristics is presented. Grain diameter and thickness of the passivation layer are of particular significance determining its suitability for the use in pyrotechnics and rocket propellants.

Tab. 1. Properties of aluminium powder depending on the preparation method [5]

Preparation method	Grain shape	Average grain size, [μm]	Bulk density, [g cm^{-3}]	Al_2O_3, [wt.%]
Air atomization	oval with rough surface	20 - 200	0.73 - 1.24	0.1 - 1.0
Inert gas atomization	spherical	45 - 100	0.5 - 1.4	0.1 - 1.7
Condensation from gaseous phase	spherical	0.2 - 0.5	-	1
Crushing of brittle alloys Ni-Mg	sharp irregular	40 - 2000	-	-
Dry grinding	flake	45	0.27 - 0.41	2 - 21
Granulation	oval	500 - 5000	1.5 - 1.8	0.5 - 13
Granulation in water	disc	500 - 20000	1.5 - 1.7	< 13
Grinding in the liquid phase (paste)	flake	45	-	2 - 20

Determining grain diameter is possible by application of several methods described in the literature of the subject, while estimation of thickness of the passivation layer poses a serious analytical problem. Amongst methods of obtaining aluminium powder presented in Table 1 there are two which are most interesting: condensation from a gaseous phase and inert gas atomization. These methods permit obtaining grains of small diameter and very thin passivation layer.

3. Zirconium powder

High chemical activity of the active zirconium powder makes its production a complex process. It reacts, among other things, with oxygen, nitrogen, carbon, carbon oxide, carbon tetrachloride and water vapour. Also, it is much more susceptible to ignition than aluminium powder because the structure of its passivation layer is less compact. Therefore, in high temperature, aluminium melts before it reacts with an oxidizer while zirconium powder ignites and the generated thermal energy causes melting of the inside of grains. Most frequently, zirconium powder is obtained by one of the following methods determining its physicochemical properties. These are methods based on:

- reaction of zirconium granules by hydrogen in high temperature and their further comminution to the form of fine powder and water desorption:

$$Zr + H_2 \rightarrow ZrH_2$$

$$ZrH_2 \rightarrow Zr + H_2$$

- reduction of potassium hexafluorozirconate(IV) by metallic magnesium or sodium in an inert gas atmosphere at temperatures from 800 to 900 °C:

$$K_2ZrF_6 + 4\ Na \rightarrow Zr + 4\ NaF + 2\ KF;$$

- reduction of ZrO_2 by metallic calcium or calcium hydride (CaH_2) carried under argon atmosphere at temperatures from 1000 °C to 1100 °C:

$$ZrO_2 + 2\ Ca \rightarrow Zr + 2\ CaO$$

$$ZrO_2 + 2\ CaH_2 \rightarrow ZrH_2 + 2\ CaO + H_2$$

  Zirconium hydride obtained by reaction with CaH_2 is washed with water in order to eliminate impurities related to the presence of $Ca(OH)_2$, because this combination is more resistant to oxidation by oxygen from the air than zirconium powder;

- electrolysis of zirconium halides in a salt melt; best results are obtained by carrying out electrolysis of

K_2ZrF_6 in molten KCl or NaCl; a mixture containing 70 wt.% and 30 wt.% KCl and K_2ZrF_6, respectively, melts at 727 °C, and the electrolysis can be conducted at (747 – 797) °C.

$$K_2ZrF_6 \rightarrow ZrF^{2-}_6 + 2K^+$$

cathode $Zr^{4+} + e^- \rightarrow Zr^{3+} + e^- \rightarrow Zr^{2+} + 2e- \rightarrow Zr^0$

anode $4 F^- + 4 KCl \rightarrow 2Cl_2$

This method enables obtaining zirconium powder with grain diameters ranging from 50 to 200 μm;

- using the amalgam - $ZrCl_4$ being the initial material is reduced by K-Li(Hg) amalgam with K/Li= 1:4 used in an excessive amount at 400°C:

$$2\ K\text{-}Li(Hg) + ZrCl_4 \rightarrow Zr(Hg) + 2\ KCl + 2\ LiCl$$

Residues of lithium, potassium and mercury are eliminated by sublimation under lowered pressure at 1400 °C. In this powder, typical contaminants are: 60 ppm oxygen, 30 ppm nitrogen, 500 ppm carbon, 130 ppm iron, 700 ppm nickel, 200 ppm titanium, 100 ppm magnesium and 500 ppm silicon.

Zirconium powder is characterized by very low resistance to electrostatic discharge – approximately ESD 0,5 mJ - which requires maintaining special safety conditions while working with this material. For instance, using inappropriate garment can easily result in generating an electrostatic discharge of 20 mJ.

Zirconium hydride powder used in specialty pyrotechnics and rocket propellants is characterized by grain diameter ranging from 2 μm to 6 μm, hydrogen and hafnium contents of approximately 1.8 wt.% and 2.5 wt.%, respectively, and ignition temperature of 270 °C. Characteristics of zirconium powder for applications mentioned above are specified in detail in the relevant standard [6]. Chemical composition of the reference rocket propellant used by NASA: 52 wt.% zirconium powder, 42 wt.% potassium perchlorate, 5 wt.% rubber bonding agent (Viton "B") and 1 wt% graphite with particle size < 1 μm [6].

Zircon ore usually contains hafnium which is the main contaminant. It was observed that when concentration of hafnium exceeds 3 wt.%, lowering of the zirconium powder susceptibility to ignition is noted [8]. This occurs also when hydrogen is being absorbed by zirconium powder or zirconium hydride. Another important characteristic of rocket propellants is quantity of thermal energy being released depending on the weight of the oxidizer used while taking into consideration concentration of the hydrogen contained in zircon. Also, sharp edges of grains - those of reducing agent as well as oxidizer - enhance activation of pyrotechnic mixtures or propellants, therefore ball mills are not recommended for comminution of their ingredients. As already said, estimation of thickness of a thin passivation layer in the aluminium oxide poses a serious analytical problem. In zirconium powder, after determining the surface by BET method, it is possible to determine the oxide phase by the temperature programmed reduction by hydrogen or carbon oxide and to calculate thickness of the passivation layer on this basis [7].

It is also possible to lower ignition sensitivity of zirconium powder by reaction with hydrogen or by applying other methods of deactivating its surface. Such methods include coating of the powder surface with metallic aluminium or microencapsulation by forming a thin polymer film on the surface of powder grains. This can be done by a chemical (polycondensation or polymerisation) or a physical (vapour condensation or microencapsulation in the fluidized phase) process. The above method was adapted for microencapsulation of aluminium powder with grain diameter from 5 to 20 μm using an organosilicon bond to form a substrate for a protective layer [8].

In Table 2 chemical composition of selected rocket propellants containing zirconium powder is presented.

Tab. 2. Chemical composition (wt.%) of some rocket propellants containing zirconium powder [9]

Mixture component	A	B	C	D	E	F
Aluminium	20	2.0	-	-	-	-
Zirconium (22 μm)	-	35.6	37.5	30	40	30.6
Ammonium chlorate(VII)	50	42.4	42.5	30	30	44.4
PTFE (Teflon)	15	5	5	20	15	10
Viton A (bonding agent)	15	15	15	20	15	15

Legend: A, B, C, D, E and F denote specified mixtures of rocket propellants.

The above mixtures were tested at (-54, 21 and 74)°C. It was observed that with mixtures B, C and E the model rocket ascended to the height of ca 11 km while that in which mixture A was used - to ca 8 km. Combustion of the propellant in which zirconium with smaller grain diameter (i.e. 5 μm instead of 22 μm) is used, is almost three times quicker. It was also demonstrated that the speed of combustion as well as the height reached were significantly influenced by the type and concentration of the bonding agent and the propellant preparation method.
The main physicochemical characteristics of solid rocket fuels containing as additives: zircon, zircon hydride, aluminium and aluminium hydride is shown in the work [10,11].

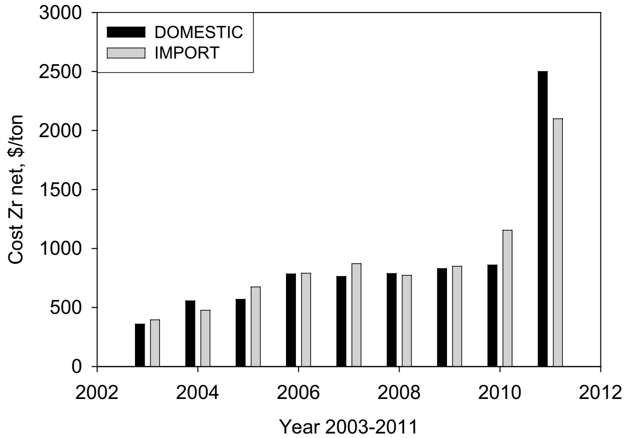

Fig. 1. The USA - fluctuations in purchase costs of 1 t metallic zirconium depending on the supplier and on time of the purchase [12]

Fig. 1 shows fluctuations in the origin related costs of purchase of 1 t metallic zirconium, in USD, in the years 2003 - 2011. Rapid price increase in 2011 can be noted when compared to previous years. Greatest global suppliers of zirconium concentrate are Australia and Republic of South Africa, while chief manufacturers of powder destined for specialty pyrotechnics and rocket propellants are the USA, Germany and France.

4. Conclusions

Aluminium powder used in specialty pyrotechnics and production of rocket propellants should be obtained by condensation from vapour phase or atomization in inert gas atmosphere. Metallic zirconium powder for these applications should be manufactured by the Kroll method consisting in reduction of $ZrCl_4$ by metallic magnesium or calcium.
Currently conducted research aims at reducing sensitivity of zirconium to electrostatic discharge (ESD) by microencapsulation or coating of the powder grains surface with aluminium or, alternatively, application of ZrH_2.

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