Study of the combustion residues for MgAl solid propellant

K. Hori[1], O. G. Glotov[2], V.E. Zarko[2], H. Habu[1], A.M.M.Faisal[3], T.D.Fedotova[4]

[1]Institute of Space and Astronautical Science, 3-1-1 Yoshinodai Sagamihara, Kanagawa 229-8510, Japan
[2]Institute of Chemical Kinetics and Combustion, Novosibirsk 630090, Russia
[3]Tokai University, 1117 Kitakaname, Hiratsuka-shi Kanagawa, 259-1292 Japan
[4]Novosibirsk State University, Novosibirsk 630090, Russia

Abstract

The goal of this research is to obtain detailed information about the condensed combustion products of MgAl solid propellant. Preliminary works have shown that the combustion completeness of MgAl particles in the flame of solid propellant is higher and characteristic sizes of the combustion are smaller as compared with propellant containing pure Al. To obtain most reliable data the sampling of the condensed combustion products was performed by two different methods: with use of the quench particle collection bomb (liquid collection method) and flow through sampling bomb (dry collection method).

The propellant under study contained 20% MgAl, 65% AP and 15% HTPB by mass. Firing runs were conducted in nitrogen at pressures 0.3 and 6 MPa. The powder of MgAl (50/50) alloy was used in the form of particles with 6-10 micron mean size. Collected particles were analyzed to determine their chemical composition and size distribution. It has been found that the metal combustion completeness is close to 100% under tested firing conditions and major part of collected particles has size less than 80 μm evidencing the absence of agglomeration. Exception was the result obtained with particular type MgAl propellant at 6 MPa, which showed strong agglomeration trend.

Introduction

MgAl alloy as a fuel in solid propellants is thought to be effective in providing flexible and high performance characteristics of solid motor. It is known that the melting and ignition temperatures of MgAl alloy are essentially lower as compared with those for pure metals. For example, when Mg content in alloy

varies in the range 37-65% mass, the melting temperature of alloy is about 720K [1]. Ignition of MgAl particles heated on the hot plate in air occurs at the temperature about 1100 K instead of 2300 K for pure Al [2]. Disruption of the mother particle and formation of small daughter particles [1,2] accompany the combustion of MgAl particles in oxidizing gas environment. In addition, at certain temperature conditions Mg can react with HCl and decrease its content in the combustion products.

First attempts to study MgAl in propellant formulations were made in 1960-70s [3,4]. In the recent researches conducted at ISAS [1] it was shown that the burning rate of the propellant containing 20% of MgAl (50:50 Mg/Al mass ratio) in the pressure range 2-8 MPa is 40% higher than that for propellant with 20% of Al. The metal combustion completeness was determined to be very high at rather short distances from the burning surface.

It is believed that for detailed characterization of metallized propellant combustion it is necessary to know the parameters of its condensed combustion products (CCP). This includes determination of the particle size distribution and chemical composition of CCP. In the present work, two techniques were employed for CCP characterization. These are the Quench Particle Collection Bomb (QPCB) method, in which the particles are collected into a thin liquid layer inside the rotating drum, and the Flow Through Sampling Bomb (FTSB) method, in which the particles are collected with a stack of wire mesh screens and aerosol filter.

The goal of the present work was detailed investigation of the properties of MgAl propellant combustion products and comparison between the results obtained by two different sampling methods.

Experimental technique

Propellant specimens preparation. Model propellants were prepared in the laboratory conditions in Japan (ISAS) and Russia (ICKC) using the same technology and almost identical components. The propellants contained by mass 65% AP, 15% HTPB based binder and 20% MgAl alloy (Mg/Al 50:50 mass ratio). Chemical analysis of MgAl particles was made by

permanganatometric method [5]. When assuming 50% content of Mg, the analysis gave the figure for total content of pure metals (Mg and Al) in the alloy: MgAl (mass %) = 85.5 ± 2.5.

The propellant formulation included 3 fractions of AP with the mass ratio for coarse/medium/fine particles equal to 6/2/1. Density of cured propellant was equal to 1630 kg/m3. The data on particle size distribution for components used at ICKC are presented in figure 1 and table 1.

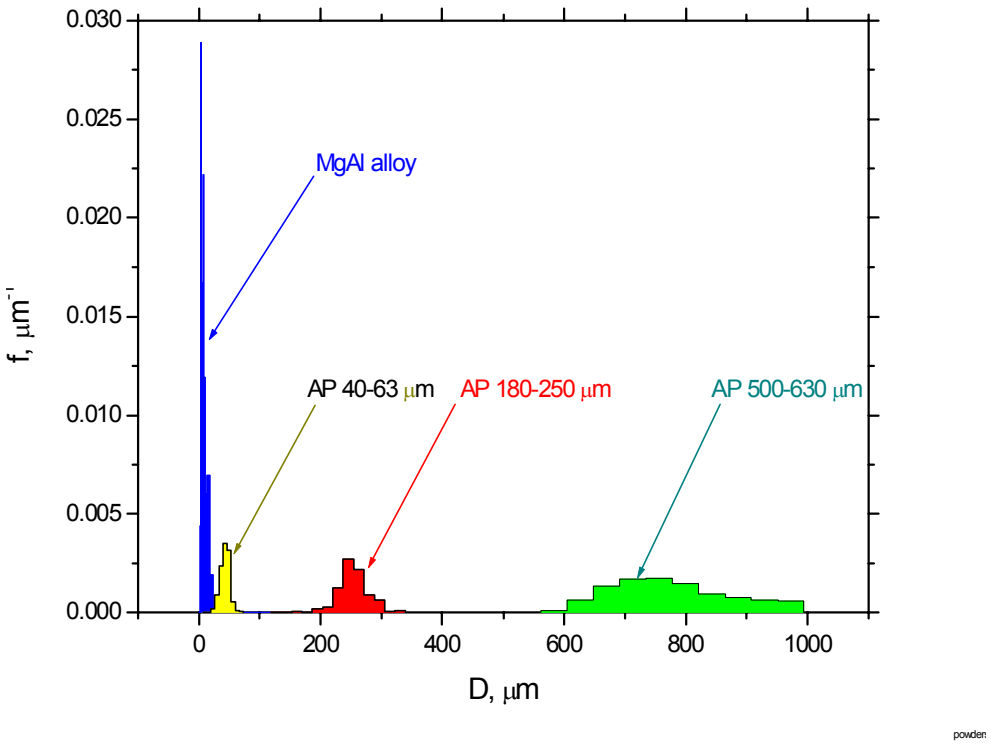


Figure 1: Mass size distribution function for heterogeneous propellant ingredients used at ICKC.

Mass size distribution function f_i (D) is defined as $f_i(D) = m_i/(M \cdot \Delta D_i)$, where m_i is the mass of particles in the i-th histogram sub-range (size interval), M is the total mass of particles, and ΔD_i is the width of i-th size interval. The $f_i(D)$ value in figure 1 is multiplied by the mass fraction of given component in the propellant formulation. Thus, the area under each curve is proportional to the mass of component in the propellant.

Table 1. Mean size D_{nm} (μm) for propellant ingredients used at ICKC.

Component	Analysis method	D_{10}	D_{20}	D_{30}	D_{21}	D_{32}	D_{43}	D_{53}
MgAl alloy	Malvern, acetone	3.7	4.1	4.7	4.6	6.3	8.8	10.2
AP fine	optical microscope	36	38	39	39	41	43	44
AP medium	optical microscope	244	245	247	247	250	253	255
AP coarse	optical microscope	742	747	753	753	764	776	782

The D_{mn} characteristic size with (m, n) order was calculated by

$$D_{mn} = \sqrt[m-n]{\left(\sum_{i=1}^{k} D_i^m \cdot N_i\right) \Big/ \left(\sum_{i=1}^{k} D_i^n \cdot N_i\right)},$$

where D_i is the midrange and N_i is the number of particles in *i-th* size range.

Characteristic sizes for AP fractions used upon manufacturing the propellant in ISAS were the following: AP fine D_{30} =30.8 μm, AP medium D_{30} = 210 μm and AP coarse D_{30} =420 μm. The MgAl particles used at ISAS had a mean diameter $D_{30} \cong 10\mu m$.

The binder used at ISAS and ICKC contained 13 % of HTPB prepolymer cured with 1% of IPDI and plastisized with 1 % of DOA. Mixing of components was performed at the temperature 60^0C. Then the propellant slurry was evacuated and cured at the temperature 60^0C during 96 hours. The propellant specimens were cut from slab of cured propellant with a tube-knife. The diameter of specimens used at ISAS was 16 mm while the specimens at ICKC were of 19-mm diameter. The height of specimens was equal to 11-15 mm. The lateral surface of specimens was inhibited with a thin layer of epoxy resin (ISAS, ICKC). In several experiments conducted at ICKC the specimens were used with diameter equal to 8 mm and height 20 mm. Their lateral surface was inhibited with Solprein^R polymer film that burned out simultaneously with the propellant.

All specimens were combusted at pressures 0.3 and 6 MPa and the initial temperature 293K. Thin layer of non-metallized propellant was placed on the top of tested specimen for facilitating ignition and preliminary heating graphite tube.

QPCB method. The QPCB method based on original work [6] has been widely used in subsequent works [7,1]. This is essentially a liquid-quench device (figure 2) consisting of the high pressure chamber with rotating drum on inner wall of which a film of liquid is formed by the centrifugal force of the rotation.

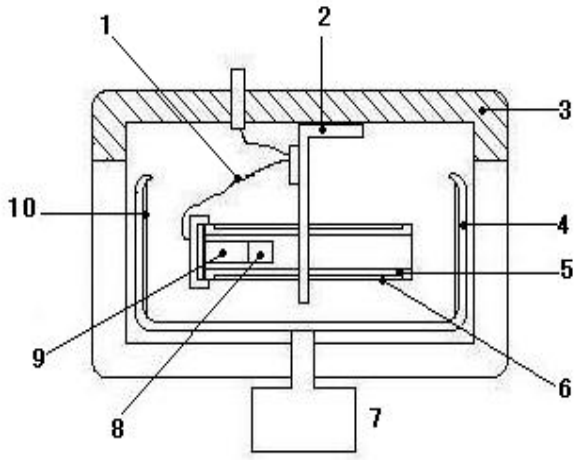


Figure 2: Quench particle collection bomb

1 - Hot-wire igniter,
2 - Steel tube holder,
3 - Cover plate,
4 - Rotating drum,
5 - Graphite tube,
6 - Steel tube,
7 - Electric motor,
8 - Propellant sample,
9 - Propellant sample holder,
10 - Liquid (rotated) layer

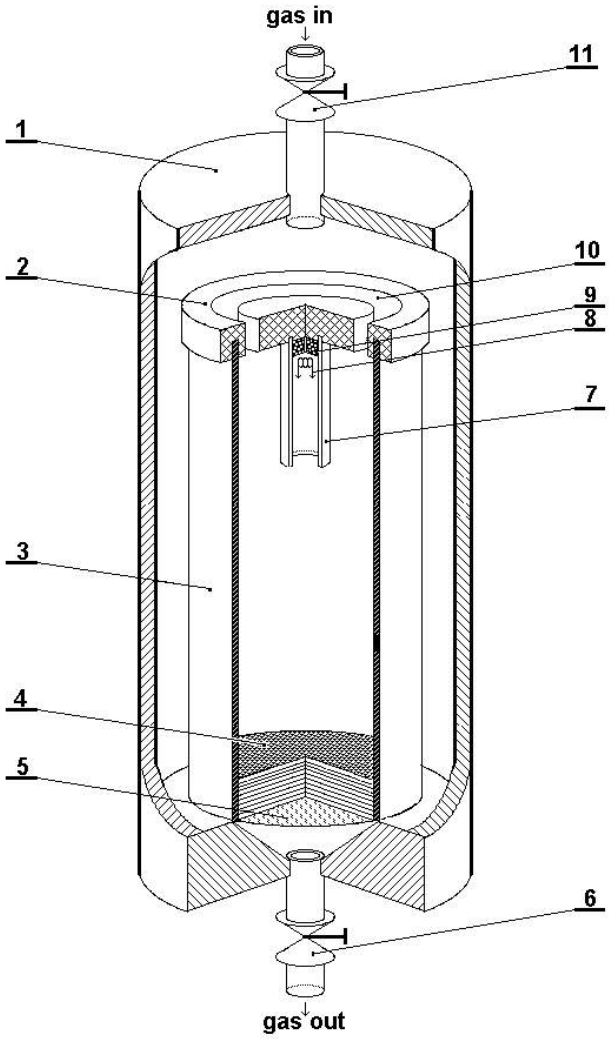
Nitrogen is used for pressurization of the chamber. The specimen is mounted horizontally on the holder with ignited surface faced towards the inside wall of drum. The combustion chamber is connected with a large volume buffer tank (not shown in figure 1), therefore the chamber pressure is kept nearly constant through the firing run. The propellant sample can be attached to the thin-wall graphite tube for prevention against the heat loss from the flame and mixing of combustion products with pressurizing gas. Quench liquid is the water solution of $NaHCO_3$ (sodium hydrogen carbonate) which effectively neutralizes HCl in dissolved combustion products. After the test, the particles were carefully removed from the drum by the series of rinsing.

The firing tests were performed in 2 geometrical configurations: with the initial (quenching) distance between the sample surface and quenching liquid layer equal to 10 mm and 100 mm, respectively. Designation of each firing run included the J letter (Japan), 2 digits (03 or 60 - pressure level in atm) and finally the letters ***a*** or ***c*** (**a** stands for 10 mm and **c** for 100 mm distance). For example, J03c means the test at 0.3 MPa and 100 mm distance to the quenching liquid.

FTSB method. The FTSB method was suggested in [8] and then successfully used for characterization of different Al containing solid propellants. The key point of the method is quenching and collecting in a special design bomb (figure 3) the full population of particles generated by the burning surface of small-size propellant specimen. The propellant specimen is mounted on the top of the bomb with the flame directed downward. The protective tube is intended for prevention of mixing the combustion products with surrounding inert gas. The linear gas velocity inside the bomb is about few cm/s that is much less than the linear gas velocity of the combustion products (few m/s). The bomb is pressurized with nitrogen and due to restricted volume of the vessel the pressure rises in the firing test depending the mass of propellant burned. All experimental data obtained are referred to the mean pressure value equal to the half of sum of initial and final pressures.

Distinctive features of the method are as follows: 1) permanent blowing the bomb with inert gas; 2) quenching the particles at different distances from the burning surface via mixing the combustion products with inert gas in spatially localized area; 3) collecting simultaneously the agglomerates (using the set of wire mesh screens) and fine oxide particles (using the aerosol filter).

The sampled particles are subjected to particle size analysis as well as to chemical analysis for determining the free metal content. The quenching distance L_{QD} for the burning particles is formally defined as the sum of the protective tube length and the length of the mixing zone for the jet of combustion products with pressurizing gas. The tests were performed in 3 geometrical configurations: without protective tube and 8 and 19 mm diameter propellant samples and with 60 mm long protective tube and 19 mm diameter propellant sample. Correspondingly, the first configuration, ***a***, provided L_{QD}=20 mm while the second one, ***b***, provided L_{QD}=48 mm and the third one, ***c***, provided L_{QD}=108 mm. The firing runs are designated similarly to the previous case, i.e. R03c stands for (Russian) experiment conducted at 0.3 MPa with L_{QD}=108 mm.



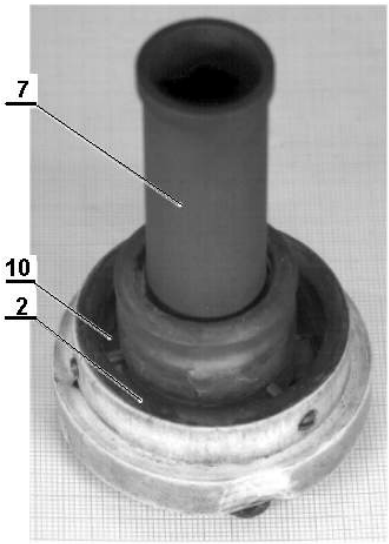


Figure 3: Chart of the flow through sampling bomb.

1 - bomb body,
2 - top cover of the cylinder 3,
3 - thin wall cylinder,
4 - stack of the wire mesh screens,
5 - filter,
6 - gas outlet valve,
7 - graphite protective tube,
8 - ignition wire,
9 - propellant specimen,
10 - ring slot for blowing the cylinder 3,
11 - gas inlet valve

Experimental Results

Geometrical structure and chemical composition of sampled CCP. The sampled CCP of larger than 60-80 μm size are presented by several types particulate. The residue contains comparable amounts of round shape gray and white color particles along with black color particles of irregular shape. The fraction of white particles decreases with increase of the residence time in the combustion gases. In addition, the residue of combustion contains irregular shape ash-like black color particles. Some of gray color particles look as broken thin wall balls. Gray color particles can be easily split by sharp knife and have complex structure. They have gray shell and white kernel inside which occupies 30-90 % of internal volume. The white color particles are hard and could not be split by knife.

Chemical analysis of sampled CCP was made at ICKC by permanganatometric method separately for the particles smaller and larger 80 μm size. The method does not allow individual determination of unburned Al or Mg but gives information about total amount of active metals in the residue. For almost all firing conditions of ICKC the amount of unburned metal was below the method sensitivity limit (0.1-0.2 mg in analyzed probe). This means that practically 100% combustion completeness of MgAl was reached. An exception were CCP collected at most unfavorable combustion conditions (P=0.3 MPa, L_{QD}= 20 mm). In this case the analysis revealed 0.7% mass of unburned metal. The conclusion about high completeness of the metal combustion was also made in ISAS on the basis of the results of X-ray diffraction analysis. Within the method resolution limit no pure metals were determined in total amount of CCP collected at ISAS.

More detailed semi quantitative analysis by X-ray diffraction method was performed at ICKC for CCP particles collected upon combustion in two extreme firing conditions: with the longest (R60c test) and shortest (R03a test) residence time. It was found that in the case of the longest residence time and highest flame temperature (P = 6 MPa, L_{QD}=108 mm) the fine particles contained comparable amounts of $MgAl_2O_4$ (spinel, cube lattice), MgO (oxide, cube lattice), and $MgCl_2 \cdot 6H_2O$ (bischofite mineral, monoclinic lattice). In the case of the shortest residence time and lowest flame temperature (P=0.3 MPa, L_{QD}=20 mm) the particles contained comparable amounts of $MgAl_2O_4$ and MgO and relatively small amounts of AlN, Al_3Mg_2 and $AlMg(OH)_{14} \cdot xH_2O$. This residue had a bad crystal structure that made difficult conducting the X-ray analysis.

Particle size distribution.

The results of the sieve analysis of the combustion residues obtained in the *ISAS experiments* under pressures 0.3 and 6 MPa are shown in table 2. It is seen that at the lower pressure the amount of fine particles (less than 32 μm) is

relatively high but, vice versa, at the elevated pressure the fraction of coarse particles is rather large.

Table 2. Mass fractions (%) of CCP collected in the ISAS experiments

Test #	Sample W, mg	TR-Total residue, mg (W%)	>180 μm, TR%	180-63 μm, TR%	63-32 μm, TR%	<32 μm, TR%	<63 μm, TR%
J03a	4,565 (100%)	562.1 (12.3 %)	0.6	2.6	10.5	86.3	96.8
J03c	4,659 (100%)	330.6 (7.1 %)	0.2	0.9	6.3	92.6	98.9
J60a	4,517 (100%)	713.6 (15.8 %)	1.7	25.5	10.9	61.9	72.8
J60c	4,758 (100%)	751.5 (15.8 %)	1.8	21.4	12.3	64.5	76.8

The results of size distribution analysis for fine (less than 32 μm) particles performed by the light scattering technique are shown in table 3. The results are presented in the form of cumulative counting function, i.e. D50 stands for the particle size (in μm) corresponding 50% of the total volume of particles in the fraction <32 μm size, etc. The interval δD (in μm) corresponds to the left and right bounds of the size range analyzed (detected).

Table 3. Cumulative counting size distribution in the fraction of particles with size less than 32 μm.

Test #	D10, μm	D25, μm	D50, μm	D75, μm	D90, μm	δD, μm
J03a	1.2	1.78	2.8	5.88	11.11	0.5-28
J03c	1.84	2.43	3.89	6.46	9.64	1.3-20
J60a	3.36	5.15	8.01	1.32	17.9	1.8-39
J60c	6.0	7.9	11.18	16.09	22.22	4.2-39

The results obtained in the *ICKC experiments* are presented below. Table 4 contains data on the relative mass fractions of CCP defined as $m_i = M_i/M_{prop}$ where M_i is the mass of CCP particles with size i and M_{prop} is the mass of burned propellant. The results of size distribution analysis for particles with size

less than 80 μm performed by the light scattering technique are presented in table 5 and figure 4. For comparison, the initial mass size distribution function for MgAl particles is shown. It is seen from figure 4 that the modal size of the size distribution function for CCP is less than that for initial MgAl particles.

Table 4. Mass fractions of CCP collected in the ICKC experiments

Test #	*P*, MPa	*r,* mm/s	m_{ccp}	$m_{<80}$	$m_{>80}$	$(m_{<80}/m_{ccp})*100\%$
R03a	0.3	3.1	0.3070	0.3067	2.717E-4	99.91
R03b	0.3	3.1	0.3175	0.3173	1.427E-4	99.96
R03c	0.3	3.1	0.3193	0.3187	5.380E-4	99.83
R60a	5.5	7.4	0.3197	0.3194	2.115E-4	99.93
R60b	5.9	7.6	0.2680	0.2677	2.982E-4	99.89
R60c	6.1	7.7	0.2297	0.2295	2.157E-4	99.91

Table 5. Mean size D_{nm} (μm) for sampled CCP particles (ICKC)

Test #	D_{10}	D_{20}	D_{30}	D_{21}	D_{32}	D_{43}	D_{53}
R03a	1.4	1.9	2.8	2.5	6.4	16.4	23.0
R03b	1.2	1.6	2.2	2.1	4.3	8.3	10.3
R03c	1.6	2.1	3.0	2.9	6.0	12.0	15.4
R60a	1.6	2.1	2.8	2.7	5.3	11.3	16.5
R60b	1.5	1.9	2.5	2.4	4.1	6.4	7.7
R60c	1.5	1.9	2.7	2.5	5.4	17.4	29.2

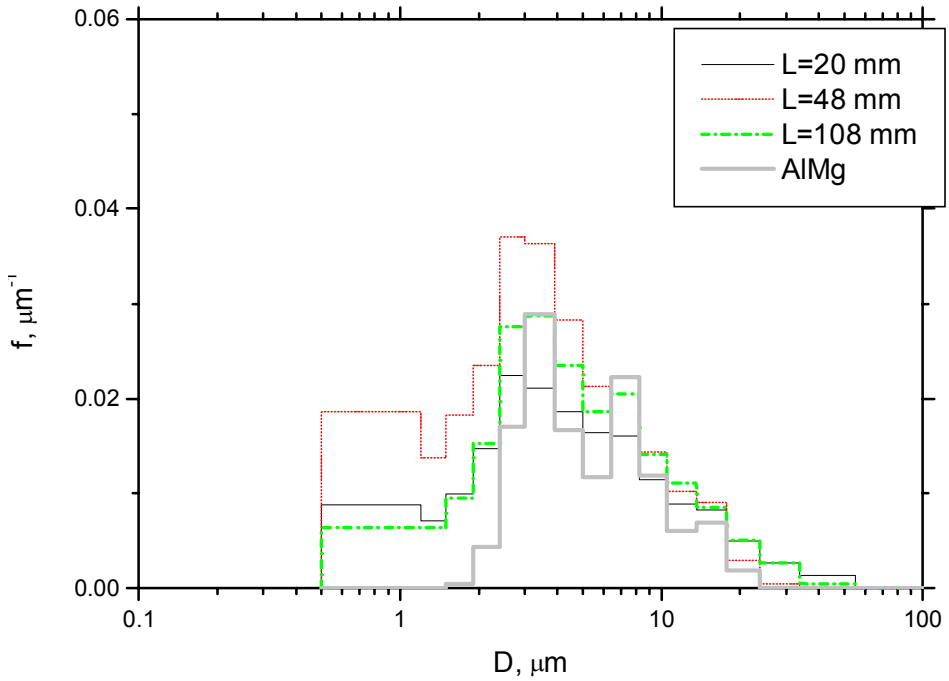


Figure 4a: Pressure 0.3 MPa

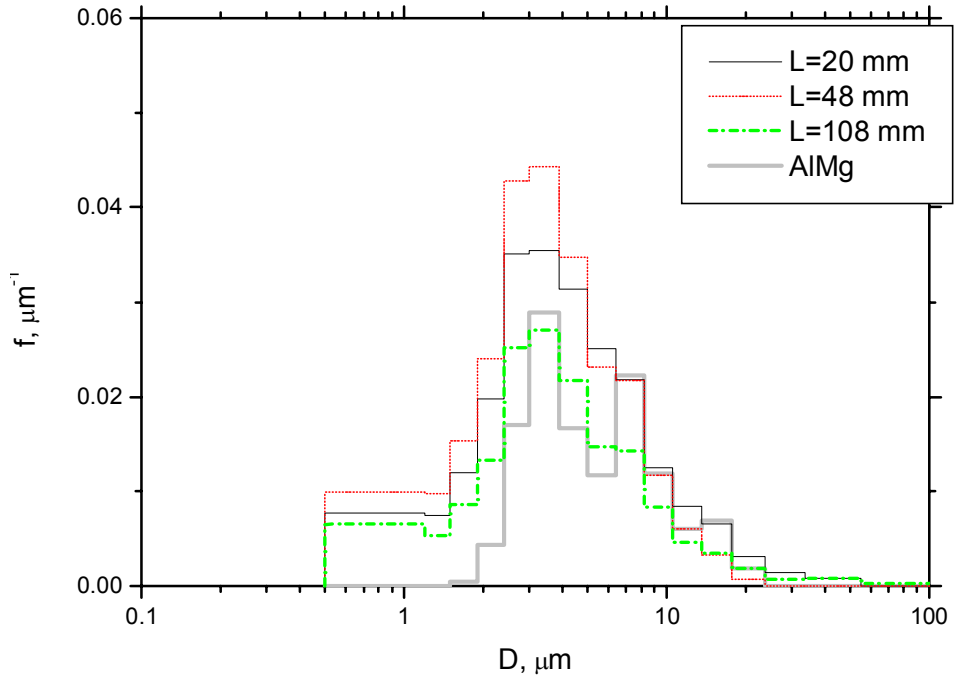


Figure 4b: Pressure 6 MPa

Figure 4: Relative mass size distribution *f(D)* of CCP particles at low (**a**) and high (**b**) pressures plotted in logarithmic scale.

Discussion

Before analyzing the experimental data obtained it is necessary to underline briefly the difference in used collection methods. This becomes most important in the case of Mg containing propellants whose combustion products are soluble in the water. The calculations by thermodynamic equilibrium code show that potentially 3 main combustion products have to be in the solid state, namely, $MgAl_2O_4$, MgO and $MgCl_2$. According to calculations the total mass of CCP is practically the same at pressures 0.3 and 6 MPa comprising about 40 % of initial mass of the propellant burned. In the case of dry collection method (FTSB, ICKC) the amount of collected CCP was equal to 23-32 % of initial sample mass that comprised 57-80 % of theoretical value. In the case of liquid collection method (QPCB, ISAS) the relative amount of CCP was equal to 7-16 % that comprised 27-61 % of theoretical value. Note that MgO and $MgCl_2$ are expected to solve in the water and theoretical value for liquid collection method is rather small (26% instead of 40%). The reasons why the methods allow collecting only part of theoretical amount of residue are not known at present time. Therefore, special efforts have to be undertaken in order to improve existing techniques for better collecting and representing CCP.

In principle, the experimental results of this work correlate well with common considerations. In the majority of the tests the collected CCP particles contained significant fraction of fine particles and comparison of original particle size distribution with that for CCP (figure 4) manifests practical absence of agglomeration of original MgAl particles. It can also be noted that the D50 size for fine particles (table 3) increases with the residence time at constant pressure. Supposedly, this is a result of aggregation of particles due to collisions in two-phase flow of the combustion products.

Another expected result is practically 100 % metal combustion completeness recorded in all experimental conditions except the test with the shortest residence time and lowest flame temperature (test R03a). However, even at such unfavorable conditions the active metal content in the residue was negligibly small (only 0.7% of total amount of collected CCP). Chemical and X-

ray diffraction analyses of the residue chemical composition gave the results, which correspond to calculated ones.

At the same time the experiments conducted in ISAS at 6 MPa revealed unexpected trend for MgAl propellants to form sizable amount of agglomerates whose mass reached 21-25 % of CCP total mass. No chemical analysis was made in this case; however, the appearance of agglomerates was similar to that for particles collected at 0.3 MPa. The mean sizes for fine particles collected at 6 MPa turned out larger than that for those collected at 0.3 MPa (D50 equal to 8 -11 μm instead of ca. 3 μm, table 3). The reasons for such difference in agglomeration trends are not clear and at present time we may only suggest that it is caused by unknown variation in physicochemical properties of the propellant specimens prepared from different batches.

Conclusions

The experiments on combustion of MgAl propellants conducted in ICKC under pressures 0.3 and 6 MPa and in ISAS under pressure 0.3 MPa revealed high completeness of the metal conversion into oxide and practical absence of the metal agglomeration on the burning surface. The combustion products of such propellants are characterized with small grain size. The experiments conducted in ISAS under pressure 6 MPa also evidenced high metal completeness but demonstrated unexpectedly strong agglomeration trend. The causes of different behavior of MgAl propellant have to be examined in the future work.

The results of the present work confirm the potential advantages of using MgAl as a fuel component in solid propellants. However, to maximize the energy storage in the propellant the content of Mg has to be minimized. Therefore, in the future work it will be of interest conducting experiments with MgAl powder containing 10-30% of Mg. For those propellant formulations it will be necessary to measure the ignition delay time and determine the burning law as well as to examine the agglomeration behavior at different pressures.

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