Characterization of Aluminum Powders I. Parameters of Reactivity of Aluminum Powders

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Summary

For testing the determination of the reactivity of aluminum powders it is proposed to use the following parameters: temperature of the beginning of oxidation, maximal oxidation rate, degree of transformation (degree of oxidation) of aluminum, relative thermal effect. Parameters for an evaluation of the reactivity of powders were chosen following the analysis of results of a non-isothermal oxidation of powders of different grain size under conditions of programmed heating (the oxidizer being air). According to the proposed method of testing, the sample of ultrafine powder UFAP-4 produced by the electrical explosion of wires has the highest reactivity among the studied powders.

1 Introduction

It is known that the ultrafine aluminum powders are promising materials as propellant additives[1]. The essential problems using low-dispersed powders, especially for high-metallized structures, are agglomeration, low degree of combustion and biphase losses. Using aluminum as a fuel component, it is necessary to estimate its reactivity, i.e. to find parameters that fully reflect its following behavior during the various processes. During production, storage, transportation and processing, the lowered reactivity of aluminum powders is desirable, and in the oxidation processes the high rates and degrees of transformation are necessary. Traditionally, the reactivity is understood as the content of metal aluminum in the powder[2], which does not cause any problems when using low-dispersed powders having spherical particles. With such an approach, there are difficulties in the definition of the superfine powders activity: with decrease in the grain size of the powders, as a rule, the content of metal is reduced, but the oxidation rate can increase by a factor of ten. Therefore, an actual problem is to use spherical ultrafine aluminum powders (UFAP) having a high reactivity at a rather high metal percentage.

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2 Materials and Methods of Approach

For the fast determination of the reactivity of powders, it is suggested to use the following parameters:

- Temperature of the beginning of oxidation (t_{bo}, °C),
- Maximal oxidation rate (v_{ox}, mg/s),
- Degree of transformation (degree of oxidation) of aluminum in certain temperature interval (τ, %),
- Relative thermal effect defined as the peak area under the DTA curve divided by weight gain ($A/\Delta m$, relative units).

These parameters for an estimation of powders reactivity can be obtained during the processing of the results of non-isothermal oxidation under conditions of programmed heating (the oxidizer being air).

The determination of the parameters of non-isothermal oxidation under standard conditions of programmed heating in an atmosphere of air[3] is well enough developed and is experimentally justified so that it can ensure the comparability of results and will allow to determine the reactivity of powders by several parameters.

The comparability of results of the thermal analysis of powders is provided by identical conditions of experiment: The weight of the studied samples of UFAP is ~50 mg, the

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Table 1. Properties of aluminum powders.

Nr.	Powder	Specific surface area (S_{sp}) (BET) m^2/g	a_s, μm	Content of metal (Al^0)*, wt-%	Bulk density, g/cm^3	Remarks
1	ASD-1	0.15	80.0	99.5	1.60	Particles are spherical
2	ASD-4	0.38	9.0	98.5	0.87	Particles are spherical
3	PY-87	5.91	Powder	96.0	0.315	Diameter from 2 to 6 μm, thickness 0.15 μm
4	UFAP-EC	11.00	0.20	86.0	0.21	Particles are spherical
5	Alex	12.10	0.18	94.8	–	Data from Ref. 5
6	UFAP-1	7.80	0.28	91.0	0.13	Particles are spherical
7	UFAP-4	16.00	0.13	89.0	0.11	Particles are spherical

*(Al^0) percentage of metallic aluminum

Table 2. Results of the differential thermal analysis of the aluminum powders.

Nr.	Powder	T_{bo}, °C	Degree of transfomation until 660 °C, α_1, %	Degree of transformation until 1000 °C, α_2, %	v_{ox}, mg/s (range of temperatures, °C)	A/Δm, relative units	Remarks
1	ASD-1	920	0.65	52.2	0.04 (920 – 950)	2.1	Weight 86.2 mg
2	ASD-4	820	2.5	41.8	0.05 (970 – 980)	–	
3	PY-87	580	8.0	40.5	0.025 (580 – 650)	–	
4	UFAP-EC	555	39.9	69.3	0.125 (560 – 570)	7.7	Weight 26.8 mg
5	Alex	548	39.4	45.0	0.05 (541 – 554)	–	Ref. 5
6	UFAP-1	560	23.9	74.3	0.04 (565 – 590)	7.0	
7	UFAP-4	540	50.1	78.6	0.05 (550 – 605)	8.7	

heating rate ~10 °C/min; other parameters were previously proved by numerous experiments[3,4].

The characteristics of the various powders are presented in Table 1:

- ASD-1, ASD-4, industrial aluminum powders (samples 1 and 2), Russia
- PY87 from Pechiney (sample 3), France
- UFAP-EC, obtained by evaporation-condensation in argon (sample 4);
- ALEX, obtained electrical wires explosion, Argonide Corp. (sample 5), U.S.A.
- UFAP-1 and UFAP-4, High Voltage Research Institute of Tomsk Polytechnic University (samples 6, 7), Russia

The specific surface area (S_{sp}) of the samples was determined by the BET method (high temperature adsorption of nitrogen). The content of metal was measured by the volumetric method (volume of hydrogen educed during the time of interaction of the powder with a solution of NaOH (5%)). The temperature of the beginning of oxidation was derived from the curve of the weight variation (TG) of the differential thermal analysis by Piloyan's method[3].

In accordance with the data of Table 1, it can be seen that an increasing of the specific surface area S_{sp} of these powders (the decrease of the average diameter of particles S_{sp}) decreases the metal percentage. With the increase of the specific surface area by a hundred approximately (from sample 1 to sample 7), the content of metal decreases by 10 wt-% approximately. The bulk density of powders decreases from sample 1 to sample 7 to less than 1/10.

3 Experimental Study of Powders

The results of the experimental study of the powders and the corresponding calculations are given in Table 2.

The temperature of the beginning of intensive oxidation for samples 1 and 2 exceeded considerably the fusion temperature of aluminum (660 °C). For other samples, t_{bo} did not exceed 660 °C (most considerably for sample 7, 120 °C lower). The degree of metal oxidation, α_1, in the interval from room temperature up to 660 °C for samples 1 and 2 was 3% and did not exceed 10% for sample 3. For UFAP (samples 4 to 7), the degree of transformation of aluminum into the products of oxidation in the same temperature interval exceeded 20% (the maximum was for sample 7, 50.1%). The region of the maximum oxidation rate was determined from the TG curve (region A-B) (Figure 1).

The highest oxidation rate was observed for sample 4. The samples 1, 2, and 6, 7 had comparable rates of oxidation. Samples 1 and 2 began intensively to oxidize at 920 °C and 820 °C, respectively, samples 6 and 7 started almost 400 °C lower. The relative thermal effect A/Δm is maximal for sample 7 being more than 4 times as important as for sample 1. Thus, the aluminum powders, of which characteristics and properties differ, can be characterized for their reactivity by four parameters.

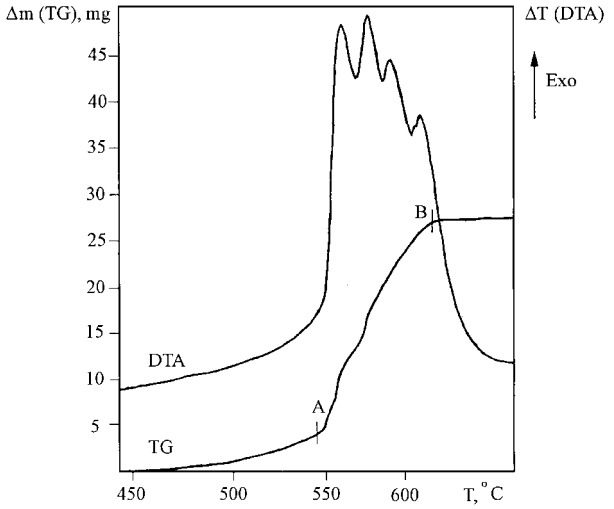

Figure 1. TG and DTA curves of sample 7 (numbering corresponds to Table 2): m = 50 mg, heating rate is 10 °C/min in air, standard is $\alpha - Al_2O_3$.

4 Discussion of Results

According to the obtained results (Table 2), the low-dispersed powders ASD-1 and ASD-4 differ from the other studied powders by the temperature of the beginning of oxidation (t_{bo}). They begin to oxidize at temperatures essentially higher than the fusion temperature of aluminum: at 920 °C and 950 °C, respectively. The change from the spherical shape of particles to the lamellar one (sample 3) leads to a decrease of t_{bo} down to 580 °C, approaching t_{bo} of ultrafine powders for which t_{bo} is 540 °C to 560 °C. The degree of oxidation α_1 (below 660 °C) strongly changes from 0.65 to 50.1 wt-% and is correlated with the temperature of the beginning of oxidation: the higher t_{bo}, the lower α_1. The degree of oxidation of aluminum in the powders from room temperature up to 1000 °C, α_2, changes in a narrower range within the limits of 40.5 – 78.6% randomly in comparison with α_1. The maximum oxidation rate v_{ox} of different powders is observed in the various temperature ranges described by higher oxidation rates. The samples (4, 5, 7) of ultrafine powders are characterized by the maximal values of v_{ox} at the lowest temperatures. It is necessary to note that low-dispersed powders oxidize with rates comparable with v_{ox} of UFAP but at higher temperatures. The values of the relative thermal effect A/Δm for UFAP changes from 7.0 to 8.7 relative units, and sample 7 is characterized by the maximum value. In contrast to other powders the first step of oxidation of sample 7 passes through some stages: It is obvious in the DTA regions of increase/decrease of the enthalpy (Figure1) that it was not known for earlier powders[5,6].

The sharp increase of temperature, probably, leads to a "start" of the endothermic processes. Among them, processes of boiling of the aluminum and binding of the nitrogen of air with the formation of AlN or AlON are most probable. Taking away the heat of the reacting system, the endothermic processes lead to a decrease of enthalpy, and this can repeat several times (for sample 7: 4 times). Due to that feedback, synergetic processes proceed at a high rate during powder combustion. The probability of occurency of the endothermic reactions with a participation of gas phase proves to be true by the data of the chemical analysis and electron microscope. In Figure 2 are shown combustion products of sample 7 which are submicron needles, while for sample 2 these are spheres. The microstructure of combustion products of UFAP-4 has strongly changed in comparison with initial powders, and the microstructure of the oxidation products of an industrial powder practically has not changed.

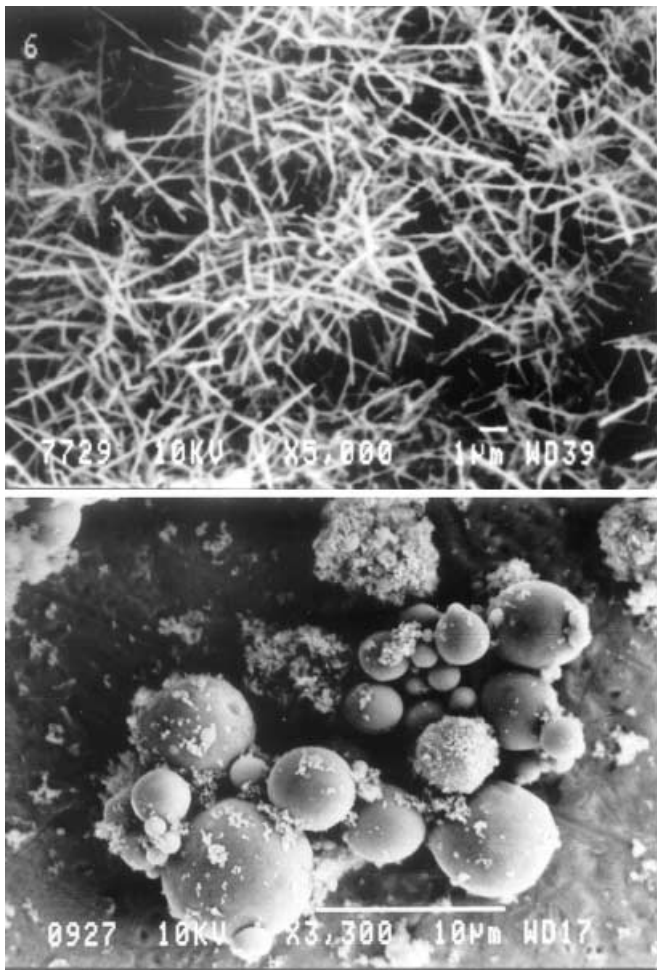

Figure 2. Electron microscope photos of oxidation products in air:
a) sample 2, magnification × 3300
b) sample 7, magnification × 5000

5 Conclusion

For diagnostics of the ultrafine aluminum powders it is necessary to use a number of characteristics which are included in the standards for usual powders: shape, distribution of particle size, specific surface area etc...[1]. At the

same time, the parameters reflecting the reactivity of powders are:

- Temperature of the beginning of oxidation
- Maximum oxidation rate
- Degree of transformation (degree of oxidation) of aluminum
- Value of thermal effect divided by a mass gain, measured under standard conditions (Fig. 1).

It is experimentally shown that such parameters can be obtained for the powders under the conditions of non-isothermal oxidation during linear heating in an atmosphere of air. The set of parameters 1 – 4 does not reflect only the activity of powders, but also their individuality, that is, it can be a test for the actual powder (Tables 1 and 2). With the use of other oxidizers the reactivity of such powders can also be determined by the above mentioned parameters taking into account the particularities of the system "aluminum powder – oxidizer". Undoubtedly, from the point of view of the use of UFAP, the parameters reflecting their structural and thermodynamic properties are – besides the kinetic parameters (Table 2) – also necessary.

6 References

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