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EFFECT OF SOME ADDITIONS ON THE CRITICAL DIAMETER AND THE RATE OF COMBUSTION OF MIXTURES OF ALUMINUM WITH GELATINIZED WATER

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Block	Italic	Transliteration	Block	Italic	Transliteration
А а	*А а*	A, a	Р р	*Р р*	R, r
Б б	*Б б*	B, b	С с	*С с*	S, s
В в	*В в*	V, v	Т т	*Т т*	T, t
Г г	*Г г*	G g	У у	*У у*	U, u
Д д	*Д д*	D, d	Ф ф	*Ф ф*	F, f
Е е	*Е е*	Ye, ye; E, e*	Х х	*Х х*	Kh, kh
Ж ж	*Ж ж*	Zh, zh	Ц ц	*Ц ц*	Ts, ts
З з	*З з*	Z, z	Ч ч	*Ч ч*	Ch, ch
И и	*И и*	I, i	Ш ш	*Ш ш*	Sh, sh
Й й	*Й й*	Y, y	Щ щ	*Щ щ*	Shch, shch
К к	*К к*	K, k	Ъ ъ	*Ъ ъ*	"
Л л	*Л л*	L, l	Ы ы	*Ы ы*	Y, y
М м	*М м*	M, m	Ь ь	*Ь ь*	'
Н н	*Н н*	N, n	Э э	*Э э*	E, e
О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

*ye initially, after vowels, and after ъ, ь; e elsewhere. When written as ё in Russian, transliterate as yё or ё. The use of diacritical marks is preferred, but such marks may be omitted when expediency dictates.

GREEK ALPHABET

Alpha	Α	α	*α*		Nu	Ν	ν	
Beta	Β	β			Xi	Ξ	ξ	
Gamma	Γ	γ			Omicron	Ο	ο	
Delta	Δ	δ			Pi	Π	π	
Epsilon	Ε	ε	ϵ		Rho	Ρ	ρ	ϱ
Zeta	Ζ	ζ			Sigma	Σ	σ	ς
Eta	Η	η			Tau	Τ	τ	
Theta	Θ	θ	ϑ		Upsilon	Υ	υ	
Iota	Ι	ι			Phi	Φ	φ	ϕ
Kappa	Κ	ϰ	κ	*κ*	Chi	Χ	χ	
Lambda	Λ	λ			Psi	Ψ	ψ	
Mu	Μ	μ			Omega	Ω	ω	

RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English
sin	sin
cos	cos
tg	tan
ctg	cot
sec	sec
cosec	csc
sh	sinh
ch	cosh
th	tanh
cth	coth
sch	sech
csch	csch
arc sin	$\sin^{-1}$
arc cos	$\cos^{-1}$
arc tg	$\tan^{-1}$
arc ctg	$\cot^{-1}$
arc sec	$\sec^{-1}$
arc cosec	$\csc^{-1}$
arc sh	$\sinh^{-1}$
arc ch	$\cosh^{-1}$
arc th	$\tanh^{-1}$
arc cth	$\coth^{-1}$
arc sch	sech^{-1}
arc csch	csch^{-1}

Russian	English
rot	curl
lg	log

GRAPHICS DISCLAIMER

EFFECT OF SOME ADDITIONS ON THE CRITICAL DIAMETER AND THE RATE OF COMBUSTION OF MIXTURES OF ALUMINUM WITH GELATINIZED WATER

A. V. Vasil'yev, V. V. Gorbunov, and A. A. Shidlovskiy
(Moscow Institute of Chemical Equipment)

It is known that the ignition and combustion of aluminum powder is substantially impeded by the presence of a strong high-melting oxide film on the surface of its particles [1, 2]. By disturbing the integrity of this film by means of any physical or chemical effects, it is possible to decrease its protective properties and, thus, contribute to the ignition and combustion of aluminum. One of the possible methods is the lowering of the melting point of the oxide film with the introduction of fluorides of the metals, which form with Al_2O_3 readily fusible complex compounds. As an example, it is possible to indicate a considerable decrease in the flash point of a mixture of $KClO_4$ with Al with the addition of aluminum fluoride [3].

The effect of fluorides of Li, Na, K and Al on the critical diameter and the rate of combustion of a mixture of aluminum powder with water [4, 5] was investigated in the present work.

A weighed sample of water, gelatinized by 3% sodium salt of carboxymethyl cellulose (CMC), was thoroughly mixed with the aluminum powder (the average particle size of the aluminum was 1 μm and was determined on a PSKh-2 instrument) whose quantity corresponded to the stoichiometric composition of $Al:H_2O=50:50$. With the introduction of the addition the weighed sample of fluoride was preliminarily mixed with the aluminum powder. The low-solubility fluorides of Li and Al has particle sizes less than 50 μm. The plastic mixture was rubbed through a screen with a mesh of 160 μm in size by a rubber stopper for obtaining small granules whose weighed sample was placed into a small glass beaker and pressed by hand to a density of 1.0-1.1 g/cm^3 $K_{compaction}=0.5-0.6$).

The ignition of the charge was realized by a nichrome spiral, heated by an electric current, sometimes with an igniting primer in whose capacity was usually used a mixture close in composition to the investigated mixture and well ignited under the conditions of the experiment.

The experiment consisted of three sections: a) the determination of the critical diameter ($d_{кр}$) and rate of combustion at atmospheric pressure (in air): combustion time in this case was measured by a timer; the length of the section of charge on which the measurement was made, was 15-20 mm; b) the determination of the dependence of the rate of combustion on the pressure in an interval of 20-100 atm. in a bomb of constant pressure in a nitrogen atmosphere; a photorecorder was used for measuring the rate of combustion; c) the determination of the completeness of the oxidation of aluminum with the combustion of the mixture in a manometer bomb under increasing pressure up to 60-100 atm.; the volume of hydrogen which was separated with the combustion of the charge was measured.

The results of the experiment concerning the effect of metal fluorides on $d_{кр}$ of the mixture of $Al:H_2O=50:50$ are shown in Fig. 1. The greatest decrease in $d_{кр}$ occurs in the case of the addition of Na and K fluorides readily soluble in water the introduction of the low-solubility fluorides of Li and Al affects the value of $d_{кр}$ less. The introduction of additions is barely reflected in the rate of combustion; in all cases it was found within the range of 0.15-0.18 cm/s.

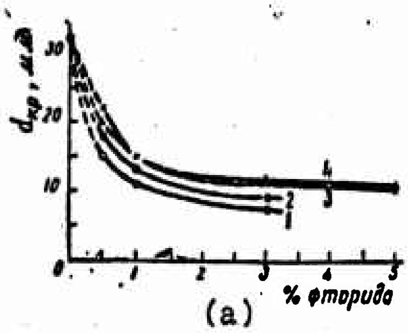

Fig. 1. Effect of the additions of metal fluorides on the critical diameter of the combustion of the mixture of $Al:H_2O=50:50$; ($\rho=1.0$ g/cm^3, H_2O+3% CMC, average particle size of Al, 1 μm). Additions: 1 - KF; 2 - NaF; 3 - LiF; 4 - AlF_3. (Points on the curves are the smallest diameter of the charge at which combustion was observed).
Key: (a) fluoride.

Also, sodium hydroxide was tested as an addition to the $Al+H_2O$ mixture. Aqueous solutions were prepared with its concentration of 0.04%, 0.4% and 0.8%, which had pHs of 12.0; 13.0 and 13.2 respectively.

The tests showed that the replacement of water in alkaline solutions leads to a significant decrease in $d_{кр}$: with a content of NaOH of 0.04% a decrease in $d_{кр}$ from 32 to 15 mm occurs. With an increase in the content of NaOH still a certain decrease in $d_{кр}$ to 13.0 and 12.8 mm respectively occurs.

The introduction into the mixture of 5% KCl not only does not decrease, but even somewhat increases (from 32 to 37 mm) the critical diameter; the mixture of $Al+H_2O$ with KCl burns very slowly and is uneven.

For the purpose of checking whether, the effect of the fluorides is specific only for aluminum mixtures, we tested an addition of LiF in a mixture of $Mg:H_2O=57:43$. The experiment showed that the mixture without the addition burns with a diameter of 12 mm, and the introduction of 5% LiF increases the $d_{кр}$ to 18 mm. Mixtures even with the addition of the fluoride and without it burn very unevenly.

To determine the dependence of the rate of combustion on the pressure charges with additions of metal fluorides in the amount of 1% with respect to the weight of aluminum[1] were used. The charge density was 1.0-1.1 g/cm^3.

As can be seen from Fig. 2, with an increase in the pressure the rate of combustion is increased; the curves have a weakly expressed saturating nature. The addition of 1% of fluorides of alkali metals (Na, K, Li) increases the rate of combustion by approximately 1.5 times, without substantially changing the nature of the dependence of the rate on the pressure. The addition of 1% AlF_3 not only does not accelerate, but even retards the combustion process.

The completeness of the oxidation of the metal was determined in the manometer bomb. Charges 20-22 mm in diameter, which had a density of 0.45-0.55 g/cm^3 ($D_{compaction}$=0.2-0.3), were burned. The stoichiometric mixture of $Mg+BaO_2$ in a 2 g amount was used as the igniter. Attempts were made to ignite under the same conditions a mixture of $(Al+H_2O)_{stoichiometric}$ without additions. The mixture was ignited with great difficulty, and combustion was reached only in two experiments; in this case the mixture was not rubbed through a screen, but was separated directly in a glass beaker, which served as the shell of the charge.

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[1] On a sample of LiF it was established that an increase in the content of fluoride in the mixture does not appear in the value of the rate of combustion and in the nature of its dependence on the pressure. The curve $U=f(P)$ for a mixture of $(Al+H_2O)_{stoichiometric}+5\%$ LiF virtually coincides with the curve for a mixture which contains 1% LiF.

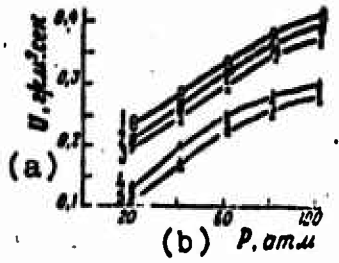

Fig. 2. Dependence of the rate of combustion on the pressure for a mixture of $Al:H_2O=50:50+1\%$ of metal fluoride ($\rho=1.0-1.1$ g/cm^3; $H_2O-3\%$ CMC; particle size of Al 1 μm). Additions: 1 - NaF; 2 - KF; 3 - LiF; 4 - without additions; 5 - AlF_3. Key: (a) U, g/cm^2 s; (b) P, atm.

The experiments showed that during the combustion of a mixture of $(Al+H_2O)_{\text{стех}}$ without additions the completeness of the oxidation of aluminum was only 44-53%. The introduction of fluorides of Li, Na, K, Al to the mixture raises the completeness of the oxidation of aluminum to 68-74%. The manometric curves of P-τ, obtained in the combustion of the mixture of $Al+H_2O$ with additions of 1% fluorides, are shown in Fig. 3. In spite of the significant attainable pressure (60-100 atm.), the combustion was slow and the total combustion time was from 7 to 25 seconds. The mixtures with NaF and KF (7 s) burned faster than the others rate of the slowest combustion was observed with the addition of LiF (13 s), and the process of the combustion of the mixture with the addition of AlF_3 was lengthened by 25 seconds, and the pressure increased only to 60 atm.

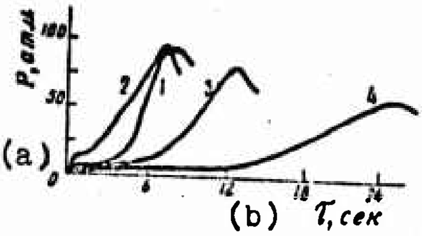

Fig. 3. Manometric curves of P-τ of the combustion of the mixtures $Al:H_2O=50:50$ with the addition of 1% metal fluorides. Additions: 1 - NaF; 2 - KF; 3 - LiF; 4 - AlF_3. Key: (a) P, atm.; (b) τ, s.

The attempt to intensify the combustion of the mixture of $(Al+H_2O)_{\text{stoichiometric}}$ in the manometer bomb by the addition to it of 5% NaCl did not succeed; this mixture could not be ignited. Testing of the mixture of $(Mg+H_2O)_{\text{stoichiometric}}$ the addition of 10% LiF in the manometer bomb showed that under conditions of elevated pressure lithium fluoride does not intensify the combustion of the water-magnesium mixture: neither the time nor the maximum pressure nor the completeness of the oxidation of magnesium were changed substantially. In conclusion, let us note that experiments on the combustion of mixtures of $Al+H_2O$, which contain greater than 3%, we did not realize the quantity of fluorides of Na and K, since such mixtures turned out to be chemically unstable: 10-15 minutes after the preparation of the mixtures containing 5% NaF or KF, they began to strongly heat-up and the full boil-off of water from the mixture occurred. One should assume that along with the reversible hydrolysis of the fluorides of $2NaF+H_2O \rightleftarrows NaHF_2+NaOH$ the process of the destruction of oxide film on aluminum proceeded here, i.e.,

$$Al_2O_3+12NaF\mathit{aq}+3H_2O=2Na_3AlF_6+6NaOH+10\ \text{kcal}^{1}$$

but the alkaline medium conditioned the energetic oxidation of the uncovered metallic aluminum after the removal of the oxide film.

Determination of the pH of aqueous solutions of the fluorides of sodium and potassium (using a LPU-01 potentiometer) gave values of 8.7 and 8.0 respectively. For the suspension of $Al(OH)_3$ prepared by us in water the pH turned out equal to 7.5. The addition to this suspension of aqueous solutions of flouorides considerably increased the alkalinity of the system. Measurement of the pH gave the following results: $Al(OH)_3+NaFaq-11.4$; $Al(OH)_3+$ $+KFaq-10.8$. A solution of LiF had a pH of 8.8, and after mixing with a suspension of $Al(OH)_3-9.4$. The suspension of AlF_2 individually had a pH of 6.9, and after combining with the suspension $Al(OH)_3-7.7$.

These experiments confirm the equations given above of reactions for the case of the fluorides of sodium (potassium) and, to a lesser degree, for lithium fluoride. Aluminum fluoride

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[1] With the calculation for Na_3AlF_6 value $\Delta H_{298}=-784.8$ kcal/mole is taken [6].

and $Al(OH)_3$, obviously, do not react with each other, and in this case a noticeable change in pH is not observed.

Finally, we prepared an 0.1 M aqueous solution of NaOH, which had a pH of 13, and with its use a mixture of $Al+H_2O(NaOH)$ was made; the gelatinizer (CMC) was not used in this case, since the Al-powder was well moistened with an alkaline solution. This mixture was ignited and burned in the manometer bomb for 5-6 seconds, after creating a pressure of 115-130 atm. The completeness of the oxidation of the aluminum was 73-74% in this case.

Conclusions

1. It is shown that the addition of 1-5% of fluorides of Li, Na, K and Al to a model mixture of $(Al+H_2O)_{stoichiometric}$ improves its inflammability and decreases the critical diameter of combustion at atmospheric pressure. The fluorides of sodium and potassium readily soluble in water exert a greater effect on the ignition and combustion processes of the mixture than the hardly water-soluble fluorides of lithium and aluminum.

2. The significant increase in pH of the aqueous solutions of NaF and KF with the addition to them of a suspension of $Al(OH)_3$ makes it possible to assume that the above-mentioned phenomena during combustion should be explained by the intense destruction of oxide film on particles of aluminum under the action of a hot aqueous solution of fluorides of sodium or potassium.

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