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INTERACTIONS OF OXIDES IN HEATING AND COMBUSTION

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Special features of the component interaction in two groups of SHS systems are investigated: I) oxide-oxidizer+oxide-reducer and II) oxide mixtures in which the reaction of formation of a complex oxide is not redox. It is shown that the components of mixtures I first transform into the components of the corresponding mixture II and only after that into the final products. Mass transfer of the reagents in all steps involves eutectic melts as well as gaseous intermediate products whose formation is caused by impurities. Basic macrosteps of the interaction processes of Ba and Sr oxides with WO_3 and MoO_3 are proposed and confirmed experimentally.

Oxide mixtures are an important class of SHS systems for both practical applications and investigations to deepen the concepts of special features of reaction of solid components under the rigorous conditions of SHS processes [1]. The present work summarizes the results of investigation of compositions reacting by the scheme: oxide 1 + oxide 2 → a complex oxide, in particular, by T_{ad} (calculated by the procedure of [2] and experiments on performing SHS (see Table 1)).

Dividing all oxide compositions into two basic groups is justified [3, 4]: I) those that are constructed on the principle agreed upon in combustion: oxidizer+reducer; II) mixtures, the interaction of whose components is not accompanied by a change in the oxidation level of the elements.

An intermediate position in this classification is taken by BaO_2+WO_2 type mixtures,reactions in which, though redox, do not permit, unlike group I, distinguishing the oxide-oxidizer and the oxide-reducer. Any composition can be associated with analogs (intended for producing the same product) from two other groups, the thermal effect and T_{ad} in the compositions of group I always being larger. Correspondingly the SHS processes in them are more vigorous and in many cases are accompanied by melting and dispersion of the specimens. On the contrary, in group II and the intermediate group the SHS processes are more quiescent, without melting of the specimens.

Compositions of Group I. Of interest are results obtained in investigating the mixtures $PbO_2+WO_2+xPbWO_4$ [6-8], in which the final product $PbWO_4$ is introduced to decrease the combustion temperature T_c and to prevent melting (for $x = 0$: $T_c = 1600$ K, $u = 4.8$ mm/sec; $x = 1$: $T_c = 1050$ K, $u = 0.7$ mm/sec; for $x > 1$ we failed to initiate SHS).

The temperature profiles (recorded using microthermocouples [7]) and the results of probing the SHS wave using synchrotron radiation [8] indicate the step character of the component interaction. On all profiles, whatever T_c, we observe a bend in the region 720-740 K and a plateau at 990-1000 K so that the reaction front turns out to be divided into several zones, in each of which their own physicochemical transformations of the initial and intermediate materials, typical of the given temperature interval, occur.

From the data of complex thermal analysis [9], PbO_2 decomposes at 570-900 K in several steps with oxygen release and formation of lead oxides. In turn, WO_2 is easily oxidized by oxygen to WO_3. Under derivatograph conditions the maximum of the oxidation rate (and of the heat release) lies near 730 K.

In heating of PbO_2 and WO_2 mixtures (in an inert gas medium) interaction occurs with heat release in two steps: at 730 and 990 K. According to the data of X-ray phase analysis, in the first step the initial materials

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TABLE 1. Results of Calculating T_{ad} and Experiments on SHS of Complex Oxides [3-6]

Composition of the initial mixture	T_{ad}, K	SHS products	
		expected	experiment
CaO_2+WO_2	2500	$CaWO_4$	
CaO_2+MoO_2	2100	$CaMoO_4$	
SrO_2+WO_2	2500	$SrWO_4$	
SrO_2+MoO_2	2100	$SrMoO_4$	
BaO_2+WO_2	2600	$BaWO_4$	
BaO_2+MoO_2	2100	$BaMoO_4$	
PbO_2+WO_2	2200	$PbWO_4$	
PbO_2+MoO_2	1400	$PbMoO_4^*$	
MnO_2+WO_2	1600	$MnWO_4^*$	
MnO_2+MoO_2	1200	$MnMoO_4$	-
$CaO_2+0.5(Si+SiO_2)$	3500	$CaSiO_3$	
$CaO_2+0.5(Ti+TiO_2)$	3500	$CaTiO_3$	
$CaO_2+0.5(Zr+ZrO_2)$	3200	$CaZrO_3$	$CaZrO_3$, ZrO_2
$SrO_2+0.5(Si+SiO_2)$	3400	$SrTiO_3$	
$SrO_2+0.5(Ti+TiO_2)$	3500	$CaTiO_3$	
$SrO_2+0.5(Zr+ZrO_2)$	3500		
$BaO_2+0.5(SiO_2+SiO_2)$	3400	$BaSiO_3$	
$BaO_2+0.5(Ti+TiO_2)$	3500	$BaTiO_3$	Ba_2TiO_4, $BaTiO_3$
$BaO_2+0.5(Zr+ZrO_2)$	3500	$BaZrO_3$	$BaZrO_3$, ZrO_2
$PbO_2+0.5(Si+SiO_2)$	-	$PbSiO_3$	$PbSiO_3$, SiO_2
$PbO_2+0.5(Ti+TiO_2)$	-	$PbTiO_3$	$PbTiO_3$, TiO_2
$PbO_2+0.5(Zr+ZrO_2)$	-	$PbZrO_3$	$PbZrO_3$, ZrO_2
$BaO2+WO_3$	1200	$BaWO_4+1/2O_2$	$BaWO_4$, O_2
$2BaO_2+WO_3$	-	$Ba_2WO_5+O_2$	$BaWO_4$, Ba_3WO_6
$3BaO_2+WO_3$	-	$Ba_3WO_6+3/2O_2$	
BaO_2+MoO_3	1200	$BaMoO_4+1/2O_2$	
$CaO+WO_3$	1370	$CaWO_4$	-
$CaO+MoO_3$	1420	$CaMoO_4^*$	
$CaO+SiO_2$	1360	$CaSiO_3$	-
$CaO+TiO_2$	1000	$CaTiO_3$	-
$SrO+WO_3$	1600	$SrWO_4$	
$SrO+MoO_3$	1600	$SrMoO_4$	
$SrO+SiO_2$	1620	$SrSiO_3$	-
$SrO+TiO_2$	1400	$SrTiO_3$	-
$BaO+WO_2$	1800	$BaWO_4$	
$2BaO+WO_3$	-	Ba_2WO_5	$BaWO_4$, Ba_3WO_6
$3BaO+WO_3$	-	Ba_3WO_6	
$BaO+MoO_3$	1800	$BaMoO_4$	
$BaO+SiO_2$	1600	$BaSiO_3$	
$BaO+TiO_2$	1500	$BaTiO_3$	Ba_2TiO_4
$BaO+ZrO_2$	1300	$BaZrO_2$	-
$BaO+Al_2O_3$	900	$BaAl_2O_4$	-
PbO_2+WO_3	1100	$PbWO_4$	-
PbO_2+MoO_3	1400	$PbMoO_4^*$	

*With heating. A dash denotes that initiation of SHS failed.

transform into the intermediate products PbO and WO_3. The final product forms in the second step, after $T = 990$ K, which coincides with the melting temperature of the lowest-melting eutectic in the system $PbO-WO_3$, namely, 993 K [10]. The investigations performed showed that the interaction of PbO_2 with WO_2 in heating and in the SHS wave occurs according to the scheme

$$[PbO_2]_s \xrightarrow{T>570\text{ K}} [PbO]_s + 1/2O_2, \tag{1}$$

$$[WO_2]_s + 1/2O_2 \xrightarrow{730\text{ K}} [WO_3]_s, \tag{2}$$

$$[PbO]_s + [WO_3]_s \xrightarrow{990\text{ K}} (\text{eutectic})_f + [WO_3]_s \rightarrow [PbWO_4]_s. \tag{3}$$

Compositions of Group II and of the Intermediate Group. The investigation is carried out on the example of Ba and Sr oxide mixtures with WO_3 and MoO_3 [5, 6]. The component interaction in SHS and heating occurs uniformly in all mixtures. The resulting products are given in Table 1.

One pronounced exoeffect is observed on DTA curves. The temperature of the onset of this effect is 643 K in the compositions with BaO and BaO_2, 768 K with SrO, and 618 K in the mixtures containing BaO and SrO oxides, which is substantially lower than the melting temperatures for the pure components. The degree of conversion on completion of the heat release is 75-100%. Simultaneously with the exoeffect we observe a decrease in weight, whose value for the mixtures with BaO and SrO is not constant but depends on the duration of stay in air. In stoichiometric mixtures of BaO_2 with WO_3 and MoO_3 the decrease in weight is practically constant and corresponds to a release of 1/2 mole of O_2 per mole of BaO_2.

With the same T_c (1300-1400 K) the burning rates of freshly prepared mixtures containing MoO_3 (u = 25-30 mm/sec) are 5-10 times larger than for mixtures with WO_3 (u = 3-5 mm/sec). The degree of conversion in the SHS processes is 97-100% (in the SrO+WO_3 mixtures is 85-87%). With increasing duration of stay in air T_c and u decrease, and after 5-15 h we failed to ignite the specimens, $T_{c\,\min} = 900$ K. It is established by investigating the components that Ba and Sr oxides practically always contain hydroxide and carbonate impurities formed as a result of absorbing H_2O and CO_2 from the air. Thus, already after 20 min of stay in air (at $T \approx 298$ K and a relative humidity of 35%) 10-15% of BaO (SrO) transforms into $Ba(OH)_2$ ($Sr(OH)_2$).

It is established by the methods of thermal analysis, static tensometry, and time-flight mass spectrometry [6] that noticeable decomposition of $Ba(OH)_2$ occurs in the interval 700-1133 K (derivatograph), and with high heating rates (900 K/sec, mass spectrometer) it is not completed even at 1400 K. At $T > 673$ K $Ba(OH)_2$ melts. However, in the presence of $BaCO_3$ the liquid phase forms already at 643 K, i.e., at the melting temperature of the eutectic $Ba(OH)_2$-$BaCO_3$ (643 K according to [11]). Before melting at 673-703 K $Sr(OH)_2$ starts to decompose, as a result of which the liquid phase appears at 768 K, the melting temperature for the eutectic $Sr(OH)_2$-SrO [12]. (Provided that the $Sr(OH)_2$ decomposition is inhibited T_m = 801-813 K.) In heating of the $Ba(OH)_2$-$Sr(OH)_2$ mixtures the liquid phase appears at 618 K.

Therefore, in all the above cases the temperatures of the onset of the interaction of Ba and Sr oxides and their mixtures with WO_3 and MoO_3 (643, 768, and 618 K) coincide with the melting temperatures of the eutectics. This conclusion was clearly confirmed by an experiment in which the SrO+MoO_3 mixture, thoroughly dehydrated in vacuum at 720-740 K, was placed in a pressurized ampule and thermally analyzed. In this case, too, the exoeffect is observed at the melting temperature of the eutectic, the lowest-melting one in this system, i.e., at 940 K (943 K according to [13]). Once the ampule was de-pressurized the temperature of the onset of interaction in the mixture returned to the previous value 768 K.

The above results agree with the following scheme:

$$Ba(OH)_2 + WO_3 \xrightarrow{643\text{ K}} BaWO_4 + H_2O, \tag{4}$$

$$\frac{BaO + H_2O \longrightarrow Ba(OH)_2}{\text{for the molecular equation } BaO + WO_3 = BaWO_4}. \tag{5}$$

Similar schemes can easily be written for all the cases considered above including peroxide mixtures and mixtures with carbonates involved in reactions.

The proposed schemes assume that WO_3 (and MoO_3) remains in the solid state during the entire process, which takes place at moderately low heating rates (for example, in the derivatograph) when the interaction, starting at 643 K (768 K, etc.), has time to be completed before the temperature is considerably larger than these values. In SHS processes, with their high heating rates, reactions of the type (4) and (5) occur in the initial step in a low-temperature region. Once high temperatures (1100-1400 K) are attained, the difference in volatilities of WO_3 and MoO_3 must have an effect, which should be related to the 5-10-fold difference in the burning rates.

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