EFFECT OF POLYMORPH TRANSFORMATION OF HMX AFTER THERMAL TREATMENT ON ITS SENSITIVITY TO IMPACT FRICTION

V.N. Lashkov, O.L. Ignatov, V.N. Lobanov, A.V. Strikanov, A. N. Shestakov
RFNC-VNIIEF

HMX after heat treatment was investigated through different methods on dynamics of inverse from the unstable form in stable or metastable. Results of differential scanning calorimetry are most indicative in studies of polymorph transition in HMX.

The analysis demonstrates, that in one day after hearting there is an essential change of crystalline structure HMX, it stabilization comes in 3-5 day/

Sensitivity to mechanical effects (to friction) valued on a standard pile driver technique.

From the data, it is visible, that, despite of completion of intracrystalline processes, the sensitivity to mechanical effects heated HMX even after long-lived endurance remains on a very high level.

Friction sensitivity of macrocrystalline and finely divided HMX after heating, which causes polymorph transition in δ-modification, are comparable with sensitivity of primary explosives (even after long storage HMX).

HMX(cyclotetramethylenetetra-nitramine, octogen) is one of the most powerful high explosives offering high heat resistance and density. HMX withstands 200°C temperature for 8 hours , and 220°C for 2 hours /1-3/. On operation HMX charges can be heated to 190-210^{0}C, e.g. when crushing hot ingots or in wells.

There are four modifications of HMX crystals (α, β, γ and δ) that are stable over various temperature ranges and differ in crystal density and response to mechanical effects /2, 3, 4, 5/. The most sensitive is δ-modification and β-modification is less sensitive.

Ref/4/ investigated the process of direct polymorph transformation of HMX from β- to- δ-modification on heating, and spontaneous reverse transition of δ-modification in stable and metastable forms. As shown by microscopic and x-ray diffraction analysis, polymorph transformations occur in macrocrystalline HMX after it has been heated to more than 165°C. Heating at 180°C ensures complete β-to-δ- modification transition.

Results of differential scanning calorimetry are most indicative in studies of polymorph transition in HMX. Analysis was performed with thermogravimetric facility Setaram TG 2400.

80-100 mg samples were placed in steel crucibles 5 mm in diameter and 8 mm height. They were heated in the air at atmospheric pressure and the temperature ranging from room temperature to 200°C at the velocity of 5-deg/ min. In the course of analysis, change in the heat flow through the sample was determined with accuracy ±0,001 mW.

As a result time- and temperature-dependence of the heat through the sample was determined. Fig. 1 shows the fragment of this relation with typical polymorph transition. In the finely divided substance temperature of polymorph transformation is changed.

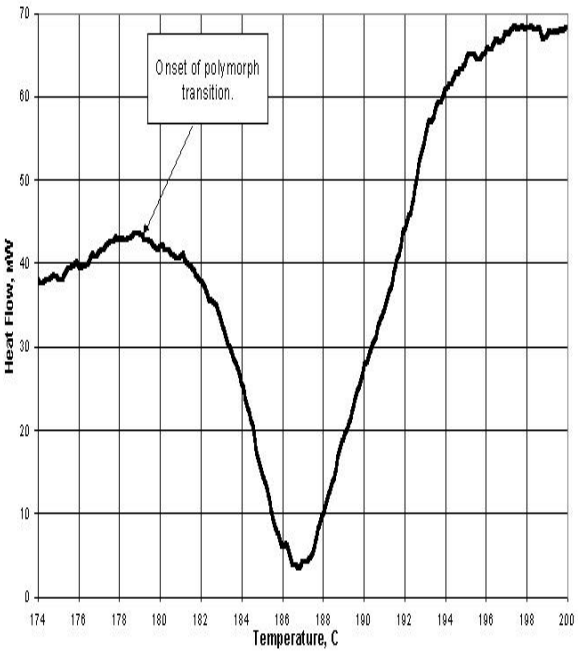


FIG. 1 FRAGMENT OF THE TEMPERATURE-DEPENDENCE OF A HEAT FLOW THROUGH THESAMPLE WITH REPRESENTATIVE POLYMORPH TRANSITION.

In the finely divided substance temperature of polymorph transformation is changed.

Temperature difference in the onset polymorph transformation of macrocrystalline and grinded (boll-milled) HMX is shown in Fig.2. It is evident from the plots that polymorph transition in grinded HMX occurs almost 10 degrees higher as compared with macrocrystalline one.

Explanation: velocity of topochemical reaction depends on defects concentration in crystal lattice (centers of the process) - in microparticles it is in unit of mass less then in macrocrystalls.

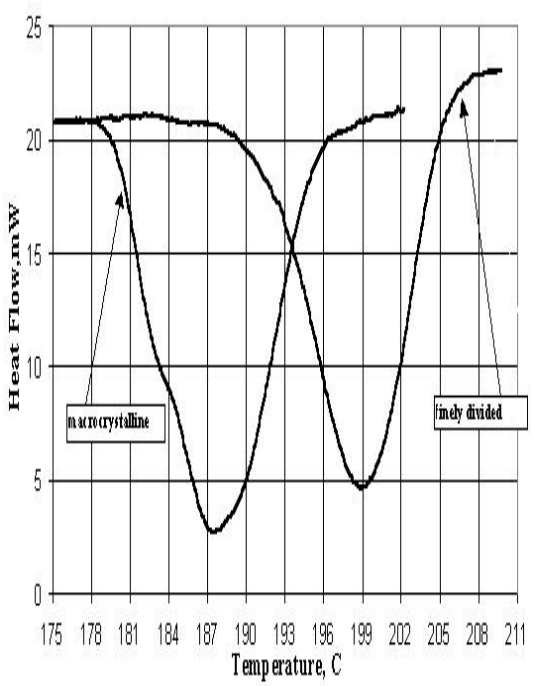


FIG. 2TEMPERATURE-DEPENDENCE OF THE HEAT FLOW FOR MACROCRYSTALLINE AND GRINDED (FINELY DIVIDED) HMX DURING POLYMORPHIC TRANSITION.

The value of specific heat absorption taking place during polymorph transition was determined by the integration of this dependence. According to experimental results, this value is 29 J/g and standard deviation - 3 J/g (number of experiments is eight). The polymorph transition temperature is 179^0C at standard deviation of $1,1^0$C. It took about 4 minutes for complete polymorph transition under these experimental conditions.

After completing the experiment, crucible with the sample was kept at room temperature for some time (time needed for reverse transition), and then experiment was repeated. In doing so, the exposure - specific heat absorption dependence was obtained for the phase portion that undergone reverse polymorph transition during storage period. This dependence is presented in Fig. 3.

The data obtained show that the portion of HMX that undergone reverse polymorph transition increases during the first three days. However, in three days reverse polymorph transition is terminated, and the value of specific heat absorption makes 60 % of the primary phase-transition heat. This testifies that initial phase composition is not recovered in transition of unstable phase into stable or metastable one. According to experimental results, average temperature of the secondary polymorph transition is 184^0C, and standard deviation makes $1,7^0$C.

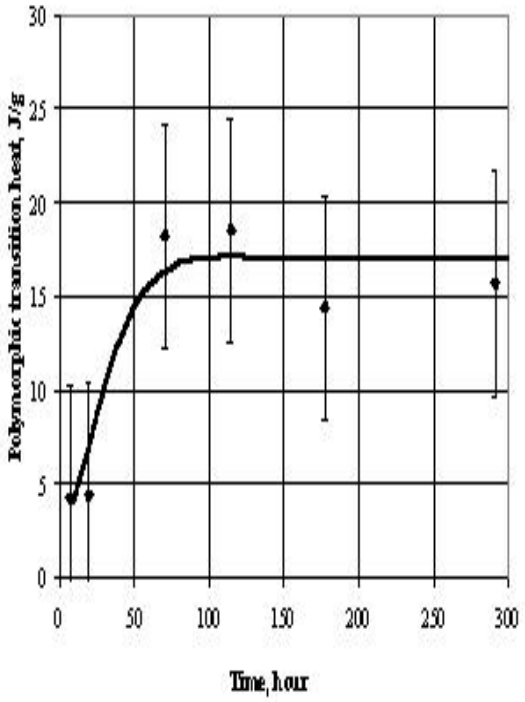
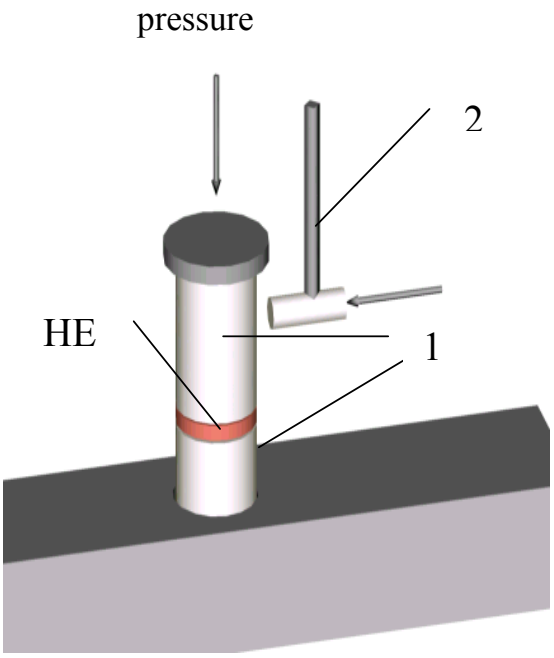


FIG. 3. EXPOSURE TIME-SPECIFIC HEAT ABSORPTION DEPENDENCE OF HMX AFTER THE FIRST POLYMORPH TRANSITION.

The authors have shown earlier /4/ that increase in friction sensitivity of HMX (shock shift) after polymorph transition in δ-modification, remains unchanged at high level for a long-time storage at room temperature (five years and more), despite of reverse polymorph transition was already terminated in first 2-3 days.

The present work continues these investigations. In the work we more detailed study friction sensitivity of macrocrystalline and ball- milled HMX.

Particularly, when determining friction sensitivity, not only low limit was determined but also dependence of explosion frequency in shock shift on the pressure of HE charge. Scheme of experiments on research of sensitivity HMX to shock-type friction (the standard test for Russia, Gost 50835-95) is shown in Fig.4.



1 - roller; **2** – impactor.

FIG.4. CIRCUIT OF DEVICE DETERMINING FRICTION SENSITIVITY IN SHOCK SHIFT.

Experimental results are listed in Tables 1 and 2. For comparison Table 3 presents data on friction sensitivity of primary explosives **TNRL (lead trinitroresorcynate)** and **lead azid** obtained in Ref. /5/ by the same technique. However, the nature of explosive transformation of HMX differs essentially from that of primary explosives. In primary explosives mechanical effects lead to detonation and in HMX they cause a flash but not detonation.

Sensitivity HMX to friction from duration heating of the sample was investigated. The samples of weight on 50 g were heated at 180C during 5, 15 and 30 minutes. For each duration the sensitivity to friction was determined. The results shown that it is enough of several minutes heating for sharp increase of sensitivity of HMX.

TABLE 1.↓FREQUENCY OF EXPLOSIONS VS. THE PRESSURE BY RUBBING SURFACES FOR MACROCRYSTALLINE HMX (FRICTION SENSITIVITY IN SHOCK SHIFT)

Pressure to rolls, MPa	*Heated 180°C*				*Not heated*		
	60	100	120	150	250	300	350
Frequency of Explosions, %	0	10	50	96	0	10	90

50% actuation point P_{50}=115 MPa (heated), P_{50}=319 MPa (not heated).

TABLE 2. FRICTION SENSITIVITY VS. DURATION STORAGE OF HMX AFTER POLYMORPH TRANSITION

HE	*Original state*	Duration storage after heating at 180°C					
		1 hour	1 day	60 days	90 days	1 year	5 years
		Lower limit of friction sensitivity, MPa					
Macrocrystalline HMX (d ~ 100 μm)	250	< 60	< 60	< 60	< 60	< 60	60
Grinded HMX (d ~ 10μm)	200	60	60	80	-	-	-

TABLE 3. FRICTION SENSITIVITY IN SHOCK SHIFT (COMPARISON THE PRESSURE CORRESPOND 0% AND 50% FREQUENCY OF EXPLOSIONS)

HE	*no heated*	*heated 180°C*	*Lead azid*	*TNRL*
$P_{50\%}$, *MPa*	320	115	180	200
$P_{0\%}$ *(Lower limit), MPa*	250	60	60	45

Conclusion.

Friction sensitivity of macrocrystalline and finely divided HMX after heating, which causes polymorph transition in δ-modification, are comparable with sensitivity of primary explosives (even after long storage HMX).

Some note based at results not presented in the report. The shock-wave sensitivity of HMX (include formulations) after polymorph transition also sharply grows, DDT-length and a critical diameter decreases (1,5-2 times, also after long storage).

During polymorph transition a let of defects appears in a crystal lattice of explosives. It results in increase of sensitivity of explosives to various kinds of an initial pulse.

There is an analogy with topochemical kinetics: the increase of concentration of the centers of reaction results give increase of speed of the process. It is possible to assume, that processes of occurrence of explosion in heterogeneous explosives submit to laws of topochemical kinetics.

We believe, that the submitted experimental results can be a subject of modeling, especially by methods of molecular dynamics.

REFERENCES

1. Dubnov L.V., Bakharevich N.C, Novels A.I. Industrial explosive substances. M: Nedra, 1988.
2. Orlova E.Yu. Chemistry and technology of HE. L.: Khimiya, 1971.
3. Orlova E.Yu., Gilin V.F.at all. Octogen - heat-resistant explosive substance. M.: Nedra, 1975.
4. Lashkov V.N., at all. Polymorphic transformations in HMX (theses of the report). Materials of the international conference " Shock waves in the condensed environments", St.-Petersburg, Russia, September 8-13, 2000, p. 89.
5. Bagal L.I. Chemistry and technology of initiating explosive substances. M.: Mashinostroenie, 1975.