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EFFECT OF PRESSURE ON THE PHASE TRANSITION BEHAVIOR OF AMMONIUM NITRATE

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Ammonium nitrate (AN) is used as oxidizer in solid propellants, explosives, gas generator systems and also as a fertilizer. AN crystallizes in five polymorphic phases that appear at different temperatures. Phase transition of AN from one polymorphic phase to another is very important as an oxidizer and also as fertilizer. During its use as an oxidizer, whether pressure plays any role in phase transition is described in this paper. High Pressure–Differential Thermal Analysis (HP–DTA) system is used for this study.

Introduction

AN is used as oxidizer in solid propellants, explosives and gas generator systems. Drawbacks of AN as a rocket fuel are low performance, low burning rates and phase transition that influence the material properties. These drawbacks and the development of the ammonium perchlorate-filled composites decreased the interest in AN for application in solid propellants in sixties and seventies [1]. New interest in AN was born when smokeless low-sensitive and ecologically harmless propellants were required, stimulating further research for understanding the phase behavior. Another primary application of AN is fertilizer. In the orthorhombic IV stage, ammonium nitrate is effective as a fertilizer, but when the compound changes phase, it is no longer viable as a fertilizing substance [2]. Ammonium nitrate crystals undergo various structural changes as the temperature increases. AN crystallizes in five polymorphic phases that appear at different temperatures [3–7]. Phase transition of AN from one polymorphic phase to another is very important as an oxidizer even at higher pressure. During its use as an oxidizer, whether pressure plays any role in phase transition is described in this paper.

Method

HP-DTA system is used for this study. This is a technique by which the thermally induced transformations in materials, in other words any thermal effect in the sample e.g. as a result of a phase transition or a chemical reaction, produced a

characteristic signal whose dependence on time just represents the measuring curve of this method [8]. Pressure is generated by a hydraulic system. The applied oil pressure is read by a thin-film pressure transducer with a high stability and having operating range 0–4 GPa absolute. A piston cylinder is used for sample holder [9]. Inside the cylinder pyrophyllite is used for sample and reference material holders. Chromel-alumel thermocouples are used to measure temperature and the temperature difference. To compensate for the heat losses from the cell a guard heater is introduced outside the piston cylinder. The temperature is maintained at the theoretical value computed from the heat transfer equations for the piston cylinder block. A pulse width modulation circuit is introduced to maintain the zero value between the experimental and set value. An ON/OFF control is introduced for the guard heater. With the help of heat transfer equations the theoretical value of temperature close to the guard heater is calculated and is considered as set temperature for it. The ON/OFF control circuit tries to bring down the difference between the experimental and the set value to zero. The pressure control is achieved by using a valve assembly. Temperature is calibrated with the thermocouple output. The conversion of the sample thermocouple output to the corresponding temperature and comparison with set temperature are done by the software. The determination of the heat of transition or the mass of the reactive sample from the area of the curve peak is a widely used procedure in DTA [8] which can be written simply as

$$\Delta Hmc = kA\Delta T_s,$$

where ΔH is the heat of transition in J/kg, m is the mass of reactive sample in kg, c is the chart speed in m/s, k is the calibration coefficient and A is the curve peak area in m^2 , ΔT_s is the differential temperature sensitivity in K/m. The calibration coefficient is related to the geometry and thermal conductivity of the sample holder and is usually determined by calibration of the system with compounds having known heats of transition. To check the system sensitivity, the both cavities are filled with alumina powder and heated. Benzoic acid is used to show the repeatability of calibration coefficient and temperature calibration. The pressure is calibrated by the phase transition of bismuth, ytterbium and benzoic acid.

Results and discussion

During the use of AN as an oxidizer, the temperature automatically raises because of burning the fuel. In the present study, three phase transitions of AN and the melting of the same are observed.

On heating from room temperature, humid ammonium nitrate transformed from phase IV into phase III (315 K), then phase III into phase II (355 K) and phase II–I (401 K) [8]. The DTA curves for this are shown in Fig. 1. The standard DTA curve reported in literature [8] is also shown in the same figure. The DTA curves obtained in our experiment under higher pressure are shown in Fig. 2. When pressure is applied both the phase transition IV to III and III to II corresponding to 315 K and 355 K shift to higher temperatures. The transition from phase IV

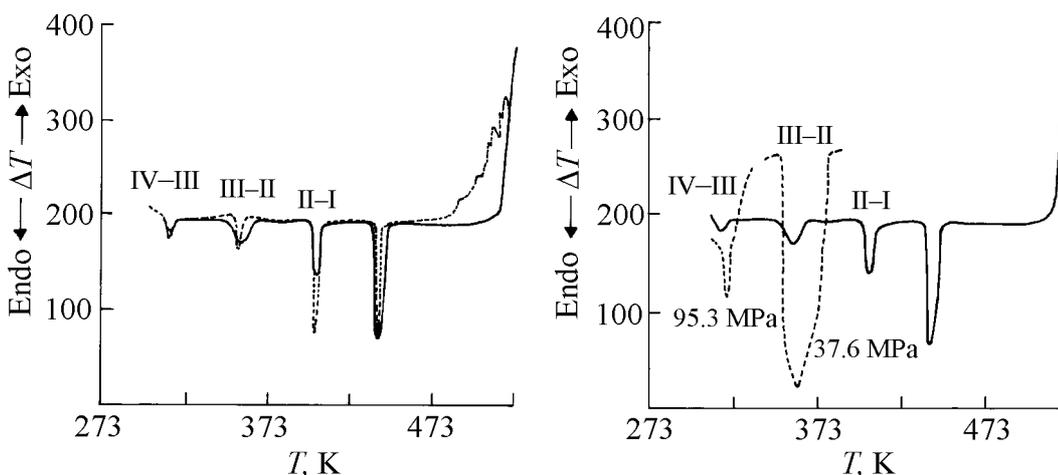


Fig. 1. The DTA curves of humid AN (--- – literature, — – experimental)

Fig. 2. Plot of temperature vs differential temperature of AN under pressure

(orthorhombic, space group ‘*pmmn*’) to phase III (orthorhombic, space group ‘*pnma*’). In the phase III to phase II transition, orthorhombic phase goes to tetragonal phase.

The shifting of the both peaks to higher temperature can be explained as follows. According to a model of Amoros [10] for phase IV the planar nitrate groups oscillate around an axis in direction of *c*. Three axes *a*, *b* and *c* are the lattice parameters correspondingly in the *x*, *y* and *z* direction. The nitrate groups lie linearly in the ‘*a*’ direction at ambient temperature (Fig. 3). Stronger oscillations with increasing temperature cause the strong expansion of ‘*b*’. As the nitrate groups deviate more and more from the linear position in direction of ‘*a*’, this parameter shrinks slightly. With an increasing parameter ‘*b*’ and a decreasing ‘*a*’, the basis of elementary cell approaches tetragonality, which is reached with the transition IV/II twisting the nitrate groups into the 45° position. But as pressure increases the nitrate group comes closer, the oscillatory path reduces as the repulsion starts. This can be seen as peaks shifts towards higher temperature so that the pressure effect is nullified by adding more heat.

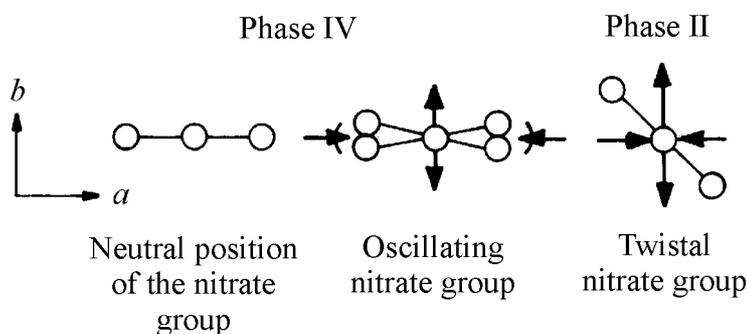


Fig. 3. Oscillation and twist of the nitrate groups on heating

Conclusion

Both temperature and pressure have effects on the phase transition of AN. This has been observed in the high pressure-differential thermal analysis system.

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