Fast crystallisation of amorphous water during the growth of a condensate film

Mikhail Yu. Efremov, Aleksandr F. Batsulin and Gleb B. Sergeev*

Department of Chemistry, M. V. Lomonosov Moscow State University, 119899 Moscow, Russian Federation. Fax: +7 095 939 0283; e-mail: gbs@cryo.chem.msu.su

Fast spontaneous crystallisation of amorphous water in the course of the growth of a condensate film at 80 K was detected after the film thickness reached a constant critical value.

Low-temperature condensates are films produced by condensation of vapours onto a cold surface. This process is characterised by an extremely high rate of cooling and can result in a metastable state of the substance and in special properties of the condensate films. Various size effects are typical of such objects. In this work, we describe fast crystallisation of an amorphous phase during the growth of a water condensate film. This effect occurs when the growing film thickness increases to a particular value.

The experiments were carried out using an original low-temperature thin-film differential scanning calorimeter. The reactor of the setup was evacuated with oil diffusion and cryogetter pumps to a vacuum of 0.1 Pa or lower. The measuring unit was a massive copper cylinder (thermostat) with two soldered copper plates (sample and reference plates) placed inside of the reactor. A differential thermocouple and microheaters were arranged on the plates. Thermal effects in the film sample caused a difference between the plate temperatures, which was compensated by the microheaters. The heat effects can be calculated from the voltage and the current in the heater. The whole measuring unit can be warmed up by the heater placed on the copper cylinder. The calorimeter was controlled by a computer.

The operation precision in the programmed heating was ±0.06 or ±0.02 K at 80 or 300 K, respectively, when the heating rate was 3 K min^{-1}. The reproducibility of calorimetric curves in an idle experiment during heating from 80 to 300 K at a rate of 3 K min^{-1} with an integration step of 1 K was as follows: the mean variation of heat power less than ±0.1 mW, the maximum variation ±0.3 mW. The absolute error of the temperature measurement during the heating at a rate of 3 K min^{-1} was within 3 K (the real temperature was always lower than the measured value) for the melting of 1-butanol condensate.

The preparation of low-temperature condensate films with predefined shapes under isothermic conditions directly in the calorimetric cell and the performance of calorimetric experiments in a vacuum are important features of this calorimeter. The calorimeter was described elsewhere.[1,2]

Typical experiment includes three stages: i, cooling of the measuring unit to 80 K with liquid nitrogen; ii, condensation of the amorphous water film in the molecular beam mode onto the sample plate (film thickness from 0.5 to 470 μm, condensation rate 6×10^{14}–5×10^{16} cm^{-2} s^{-1} or 0.01–1 μm min^{-1}) and iii, warming of the measuring unit at a rate of 3 K min^{-1}.

Spontaneous fast (several seconds) release of heat was observed when the water film thickness increased to a fixed (critical) value. The sharp exothermic effect was followed by a significant decrease of heat generation in the condensate. A typical calorimetric curve is shown in Figure 1.

A repeated fast process was observed after the first one during the continuous condensation in some experiments. The second process was less pronounced. The film undergone the fast process might partially fall off the support during the sample heating after the condensation being completed. The critical thickness of fast process was equal to 4–6 μm for the films prepared at a condensation rate of 1 μm min^{-1}. The critical thickness depends only slightly on the condensation rate: it increased no more than twice when the rate of condensation decreased by a factor of 50.
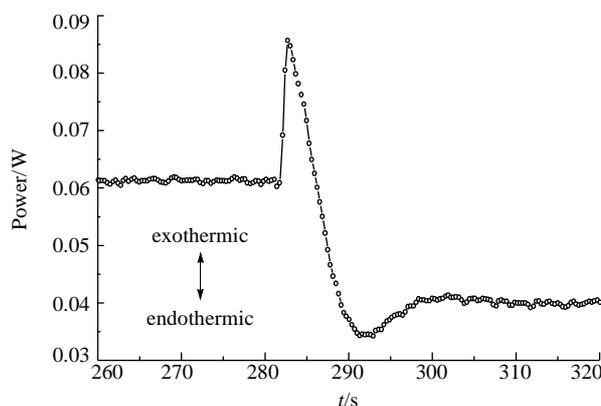

Figure 1 Dependence of the power of heat effects on the time of water condensation (a region of the fast exothermic process). The condensation rate is 0.9 μm min^{-1}.

The excess of the water film surface temperature was estimated. This value is lower than 4 K for the films of critical thickness.

The heat release during the fast process varied in the range 0.2–0.7 kJ mol^{-1}. These values are underestimated, because a portion of the released heat was masked by a subsequent decrease of background heat generation in the film. The background heat occurred due to exothermic condensation and absorption of environmental heat radiation. The condensation power is constant during the film formation; thus, it should be supposed that the decrease of the background heat generation was caused by changes in the optical properties of the film, namely, an increase of the transparency or reflectivity.

In our opinion, such a significant heat release during the fast process may be caused only by the first-order phase transition in the condensate, namely, the crystallisation of amorphous water.

The crystallisation of amorphous water films with the thickness lower than the critical value was observed during the sample heating after the film formation completed. The scanning rate was 3 K min^{-1}. The slow crystallisation (near 1 min) of the amorphous film was observed in the temperature range 163–167 K. The determined heat of crystallisation was equal to 1.2±0.1 kJ mol^{-1} (the given accuracy was calculated on the basis of 15 experiments for the confidence level 0.95). This value satisfactorily agrees with the published data, for example, 1.330±0.02 kJ mol^{-1}.[3] Thus, the heat of crystallisation of amorphous water was sufficient to provide the fast heat release during the film formation.

On the other hand, the heat of the slow crystallisation, which occurred in the samples undergone the fast process during the formation, is significantly lower. The heat of the slow crystallisation in these experiments was 0.3–0.8 kJ mol^{-1}.

Thus, it should be concluded that the sharp heat release during the water film formation is caused by the spontaneous high-velocity crystallisation of the amorphous condensate which propagated through a considerable part of the sample. A similar process during the growth of amorphous condensates of Sb, Bi and some metals, so-called spontaneous explosive crystallisation, has been observed earlier.[4] Furthermore, spontaneous explosive
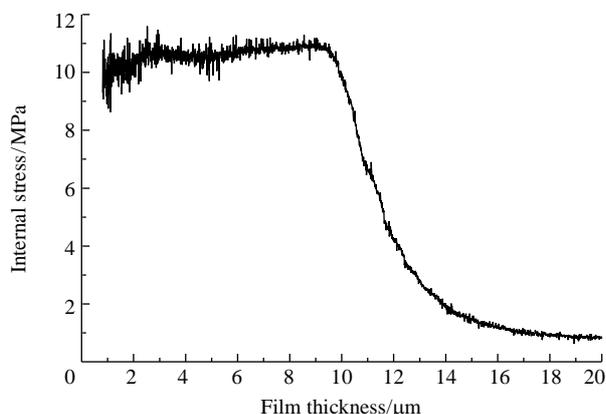
Figure 2 Dependence of the internal stress in the amorphous water condensate on the film thickness during the condensation. The condensation rate is 0.4 µm min⁻¹.

chemical reactions in the co-condensates of reagent vapours during their formation are well known.[5]

Previously, it has been demonstrated that spontaneous explosive reactions in the chemically active co-condensates can be initiated by the crack formation in the samples.[6] As a rule, condensate growth was accompanied by the generation of an internal mechanical stress in the film. This stress causes the crack destruction of the condensate film with the thickness which is equal to or greater than the critical value. This fact can initiate a chemical reaction or crystallisation propagating in the autowave mode.[7]

The applicability of the above model to the effect described here was tested as described below. The same amorphous water films were prepared in the cryotensimetric setup described earlier.[8] This setup allows the measurement the internal mechanical stress in growing low-temperature condensate films. The conditions of sample preparation in the calorimetric and tensimetric setups are comparable. The typical dependence of the internal mechanical stress on the thickness of a growing film is presented in Figure 2.

A significant decrease of the internal stress was observed when the condensate film attained the critical thickness. At this time, the formation of a crack network was detected on the film. The critical thickness determined by the heat release and that one by the crack network generation differs from each other less than 2 times. Such difference may be caused either by an error in the absolute thickness of the condensate film, determined in the tensimeter ($-50\% + 100\%$) or by the difference in the shapes of the condensate films produced in the mentioned setups.

Thus, it should be concluded that the high internal mechanical stress causes the film degradation by cracks when the thickness of the growing water condensate reaches the critical value. The crack generation may, in turn, initiates the crystallisation of the amorphous film. It is reasonable to suppose that both of these processes (degradation and crystallisation) are interconnected by a positive feedback to generate autowave explosive crystallisation of the amorphous water condensate.

References

1 M. Yu. Efremov, A. F. Batsulin and G. B. Sergeev, *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1999, **40** (3), 180 (in Russian).
2 G. B. Sergeev, M. Yu. Efremov and A. F. Batsulin, *Proceedings of the European Conference on Thin Organised Films*, Germany, 1998, p. 332.
3 A. Hallbrucker and E. J. Mayer, *Phys. Chem.*, 1987, **91**, 503.
4 V. A. Schklovskii and V. M. Kuz'menko, *Usp. Fiz. Nauk*, 1989, **157**, 311 (*Physics-Uspekhi*, 1989, **32**, 163).
5 V. S. Komarov, M. Yu. Efremov and G. B. Sergeev, *Mol. Cryst. Liq. Cryst.*, 1992, **211**, 445.
6 M. Yu. Efremov, V. S. Komarov and G. B. Sergeev, *Mol. Cryst. Liq. Cryst.*, 1994, **248**, 111.
7 V. V. Barelko, I. M. Barkalov, V. I. Gol'danskii, A. M. Zanin and D. P. Kiryukhin, *Usp. Khim.*, 1990, **59**, 353 (*Russ. Chem. Rev.*, 1990, **59**, 205).
8 M. Yu. Efremov, *PhD Thesis*, Moscow State University, Moscow, 1995 (in Russian).