OBSERVATIONS OF HETEROGENEOUS NUCLEATION OF WATER VAPOR ON A COLD SUBSTRATE

HIDEO SHINAGAWA, KIKUO OKUYAMA
AND YUJI KAWAMURA

Department of Chemical Engineering, Hiroshima University,
Higashi-Hiroshima 724

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Introduction

Heterogeneous nucleation of water vapor is encountered in various low-temperature industrial processes and during the formation of artificial rain and snow in the atmosphere. In the latter case, a large number of studies have been conducted on the activation of fine foreign particles as silver and lead iodide in various supersaturated vapors²⁾. But no investigations of heterogeneous nucleation of water vapor on metal substrates such as copper and steel, which are the materials used in cold traps and condensers, have been made in spite of its industrial importance.

In this study, the appearance of liquid or solid condensates from water vapor on a cold substrate was observed and the critical supersaturation ratios required for heterogeneous nucleation were determined.

1. Experimental Apparatus and Procedures

The experimental apparatus and method in this study are the same in principle as those reported in our previous paper³⁾, in which benzene vapor flowed through the test chamber with a cooled copper substrate and heterogeneous nucleation of benzene vapor onto the cooled substrate was evaluated under various conditions. In this study, water vapor is used instead of benzene vapor.

The test chamber was first evacuated to a negligibly small residual gas pressure. Water vapor was then introduced at low flow rates ranging from 1.6×10^{-6} to $5.5 \times 10^{-6} \text{ mol} \cdot \text{s}^{-1}$ while the coolant was circulated through the cooling cylinder below the substrate. After the vapor pressure p and substrate temperature T_s attained steady state, the substrate was cooled at a slow cooling rate (7.8×10^{-3} – $1.2 \times 10^{-2} \text{ K} \cdot \text{s}^{-1}$) by a refrigerator. The surface of the substrate was observed visually, and photographs of the condensate on the

substrate were taken at regular time intervals. The experiment lasted about 5 minutes after solid (ice) appeared. The water used was prepared by distillation followed by ion exchange.

2. Experimental Results and Discussion

The following three types of time-dependent phase transitions on the substrate were observed, depending on the vapor pressure of water supplied: (1) direct formation of solid condensate from the vapor (direct solidification), (2) formation of a liquid condensate from the vapor followed by the formation of solid condensate from the vapor (subsequent solidification), and (3) formation of a solid condensate by the freezing of the liquid condensate (subsequent freezing).

Figure 1-(a), (b) and (c) indicate schematically the variations of vapor pressure, p , and substrate temperature, T_s , with elapsed time, t , for direct solidification, subsequent solidification and subsequent freezing, respectively. In all cases, a slight decrease

Fig. 1. Typical changes in vapor pressure and substrate temperature with time

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in p was observed before the formation of the solid or liquid condensates. This was not observed in the phase transition of benzene vapors³⁾ and may be due to adsorption of water vapor before the formation of solid or liquid condensates.

Typical variations in p , T_s and the appearance of the condensate on the substrate during subsequent solidification are illustrated in **Fig. 2**. As observed in the photographs of the surface of the substrate in **Fig. 2**-(b), a number of white spots, which are most likely liquid, appeared on the central portion of the substrate surface at the time corresponding to 1 ($t=188$ s) when the supersaturation ratio S ($=p/p_{el}$), based on the equilibrium vapor pressure of supercooled liquid¹⁾ p_{el} , attained unity. The vapor pressure then decreased significantly at the same time as the small liquid droplets formed by growth of these points by condensation and coalescence. Growth continued, progressing from the center to the edge of the substrate. Just after the time labelled 2 ($t=578$ s), the vapor pressure again decreased rapidly and solid (ice) formed along the edge of the substrate. Both the number and the size of the liquid droplets then decreased with elapsed time, occurring inwardly from the brim of the substrate to the center ($t=668$ s). They disappeared completely by the time labelled 4 ($t=818$ s), while the solid crystal continued to grow. Although the presence of the ice is not obvious in the photograph, it was clearly observed by naked eye or video camera. However, in about 15% of the experimental runs the solid condensate and liquid droplets appeared at the same time. Both condensates grew simultaneously, and then the liquid disappeared while the solid continued to grow. In this case, no subsequent break point in the vapor pressure was seen, as shown by the broken line in **Fig. 1**-(b). This interesting phenomenon during condensation onto cold substrates has not been reported previously.

During the subsequent freezing process, as shown in **Fig. 1**-(c), the changes in the condensate and p up to the freezing point were the same as those observed during subsequent solidification. But, at the freezing point of the liquid, spikes were observed in both p and T_s due to the rapid liberation of heat associated with freezing and the transfer of this heat to the substrate.

For processes involving subsequent solidification and freezing of the liquid, p and T_s at the second critical point (C.P.) in **Fig. 1**-(b), (c) were adopted as the critical pressure p_c and critical temperature T_{sc} at the onset of nucleation. For the formation of liquid condensates, p and T_s at the moment when small droplets were observed and p started to decrease significantly were adopted as the apparent critical vapor pressure and temperature.

Figure 3 shows the experimental critical temperature

(a) Variations of vapor pressure and temperature

(b) Variation of condensate

Fig. 2. Variation of condensate with elapsed time for the case of subsequent solidification

Fig. 3. Critical temperature as a function of initial vapor pressure

as a function of the initial vapor pressure p_0 . **Figure 3** shows that the formation of liquid condensate tends to occur at p_0 above about 200 Pa. **Figure 4** shows the dependence of the critical supersaturation ratio S_c on

Fig. 4. Dependence of critical supersaturation ratio on critical pressure

the critical temperature for the solidification. The variation of S_c with $1/T_{sc}$ for direct solidification is different from that for the subsequent solidification and freezing processes. The difference between the relationships in the two cases may be due to differences in the nucleation mechanism. Figures 3 and 4 will be useful for predicting the solidification process of water vapor on the substrate under various conditions.

Conclusion

From the present work, the following conclusions

are drawn.

1) Water vapor initially at a constant pressure above about 200 Pa first formed liquid condensate. The liquid then disappeared or froze to form ice associated with either the subsequent solidification or freezing processes.

2) The dependence of the critical supersaturation ratio in the subsequent solidification and freezing processes on the critical temperature is different from that in direct solidification process.

Nomenclature

p	= vapor pressure	[Pa]
p_c	= critical vapor pressure	[Pa]
p_{el}	= equilibrium vapor pressure of supercooled liquid	[Pa]
p_0	= initial vapor pressure	[Pa]
S	= supersaturation ratio	[—]
S_c	= critical supersaturation ratio	[—]
T_s	= substrate temperature	[K]
T_{sc}	= critical substrate temperature	[K]

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