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THERMAL ANALYSIS STUDY ON WATER FREEZING AND SUPERCOOLING

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Water freezing and supercooling were experimentally studied by methods of thermal analysis in a water droplet of 5 mm in diameter depending on various temperatures and times of overheating and cooling rates. Degree of water supercooling was influenced by previous thermal treatment but only to a certain extent. It increased slightly with overheating temperature and time and decreased with cooling rate. Maximum found values of supercooling ranged between 12 and 13 K. Small degrees of supercooling and their changes indicate that water freezing was more controlled by heterogeneous nucleation (properties of container contact surface) than by previous thermal treatment and experimental conditions.

Keywords: *heterogeneous nucleation, thermal analysis, thermal treatment, water freezing, water supercooling*

Introduction

Water freezing and water supercooling have been intensively studied for many years due to their significance both in nature and in human activity. In nature these phenomena are connected with the formation of snow and hail and freezing of various water flows, seas and reservoirs. In human activity they play an important role in many production processes such as ice making and foodstuffs freezing and their storage. Water supercooling also became an important subject of studies related to better understanding of aforesaid processes as well as plant behavior and mortar and concrete hardening under natural and artificial freezing [1–4]. Understanding processes connected with water freezing and ice formation and their control can contribute to both early warning at weather disaster (heavy snowfall) and finding appropriate conditions under which it can be possible to affect water freezing by means of supercooling control. It means to initiate water freezing at small supercooling and vice versa to prevent water to freeze at high supercooling. There is no doubt about the economical benefit if realised under what extent these processes happen in nature and industry. Moreover, statements have recently appeared, in connection with the Mpembo effect, that thermally treated water could freeze more easily than untreated water [5, 6].

Water is an uncommon compound which exhibits some very extraordinary properties and strange behaviour. Its properties considerably differ from those to water related chemical compounds. It concerns a relatively high boiling point, exceptional large specific heat capacity and surface tension and anomalous ability to dissolve both ionic and polar compounds. Impurities solved in water decrease both its melting and boiling temperatures. Unlike most other compounds water expands as it freezes. It is believed that the reason for such properties is a great dipole moment in the water molecules and creation of attractions among them. Water molecules form an infinite hydrogen-bonded network, which gradually changes to water clusters with 5-fold symmetry as temperature decreases [1, 2].

Water supercooling and ice formation have been theoretically analysed within nucleation theory [7, 8]. Formation of the ice phase can be described by homogeneous nucleation if no foreign nucleation centres are present. However, this is a rare case in nature, because microscopic particles of solid phase are always present in water and together with the surface container act as nucleation centres. So the ice formation should be described by heterogeneous nucleation. Observations of homogeneous nucleation are performed in laboratory experiments when the supercooling depending on cooling rate and previous thermal treatment is measured in small droplets free of solid particles. The droplets are produced as clouds or are dispersed in oil without any contact with container surface [9]. The found supercooling in these droplets ranged between 30 and 40 K and increased with decrease of droplet size. In real experiments the following measuring arrangements can be used: *i*) Water solidification is initiated by a mechanical shock when supercooled water droplets strike a solid supercooled target [9]. *ii*) Measured water is placed in

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a container and the most important parameter affecting the nucleation is the wettability of the container surface. *iii*) Water is confined to porous material with pores several nm in diameter [10].

This paper deals with experimental study of water supercooling by methods of thermal analysis. Its aim is to determine water supercooling depending on temperature and time of overheating and on cooling rate and to discuss the obtained results. The measurements were performed in a water droplet placed on a polished quartz plate under exactly defined experimental arrangement, reproducible cooling rate, droplet size and conditions of thermal treatment. In our laboratory influence of molten state (controlled by temperature and time of overheating and cooling and heating rates) on supercooling of some molten halide was studied [11]. Theoretical and experimental know-how of these measurements were used in the research into water supercooling.

Experimental

Water supercooling was determined by a direct temperature measurement during cooling of the droplet of distilled water by a method similar to that described in [11]. For this study a Linkam THMS 600 heating and cooling stage was used. For all the measurements distilled water of the same batch deposited in a separated container was used. In order to measure water supercooling an arrangement was designed and the following procedure was developed and used: The droplet of distilled water of about 5 mm in diameter was set on a quartz plate placed in the stage and thermally treated. For every measurement new water was taken from the container. The water droplet was heated up or cooled down from room temperature to an asked overheating temperature and held at this temperature for a required time. Then the stage was cooled down to –40°C and after solidification finished the temperature was again increased. Overheating temperatures span within the range of 5 and 90°C. Overheating time were up to 490 min. The cooling rates ranged between 1 and 90 K min^{-1}. The measuring thermocouple, 0.4 mm in diameter, was located at the centre of the droplet. The temperature was measured and recorded every 1 s using an Ahlborn 2290-8 Almemo.

During measurement we tried the geometry of arrangement – droplet size and its location on the plate, location of the plate in the stage and location of the thermocouple in the centre of the droplet – not to be changed.

In the measurements at temperatures above 40°C water was tempered outside the stage in a bulb with a reflux condenser and only after required time it was transferred onto the quartz plate.

Results and discussion

During pilot measurements open and closed vessels of various materials such as silver, polyethylene, aluminum foil pure and covered by Teflon and silicon films of different compositions were used. Temperature was measured by a thermocouple placed either direct in water or on the contact between stage and the bottom of the vessels. The measurements were performed repeatedly in the same water droplet, water was refilled to the initial volume or so far not treated water was used. During these measurements both small reproducibility in levels of supercooling and small dependence of supercooling on thermal treatment were found. These were ascribed to the influence of the experimental arrangement, such as wettability of the vessel surface, different volume of water droplets and their changes due to water evaporation and ice sublimation, pollution of water by leaching of vessels surfaces, absorption of gases of the air or by degassing the water at higher temperatures. It seemed that both the factors mentioned above and character of nucleation produced a greater effect on supercooling than that of applied thermal treatment. Only after these examinational measurements the final experimental arrangement and procedure presented in the previous section were designed. In this proposal we tried both to decrease the contact array of water with the container surface in order to restrict its impact on ice nucleation and to use the droplets of the same size.

The scan of temperature on time during the measurement of water supercooling is shown in Fig. 1. After thermal treatment at 32.5°C for 2400 s, water droplet was cooled down with a rate of 10 K min^{-1}. The sharp peak on the cooling part of the curve starting at a temperature of –10.9°C represents water freezing temperature while the plateau on the heating part at 1.6°C is ice melting.

The dependence of the degree of water supercooling on overheating temperature under a constant cooling rate of 10 K min^{-1} and overheating time of 30 min is shown in Fig. 2. At a very low overheating of 5.4°C, the level of supercooling was about 10 K. The degree of supercooling increased with overheating temperature up to 60°C when supercooling reached a value of about 13 K. With further overheating the supercooling did not increase and remained approximately the same. In the monitored range of overheating temperatures the degrees of supercooling only changed by 3 K.

The dependence of the degree of water supercooling on overheating time at a constant cooling rate of 10 K min^{-1} and overheating temperature 70°C is shown in Fig. 3. With an overheating time up to about 200 min the supercooling enhanced and then it

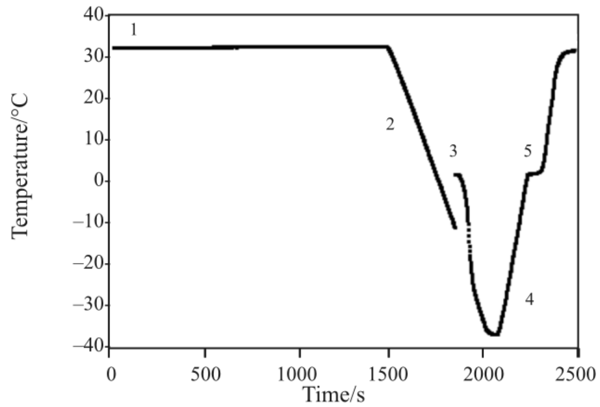

Fig. 1 The time dependence of temperature during the measurement of water supercooling, 1 – thermal treatment at 32.5°C, 2 – cooling at a cooling rate of 10 K min^{-1}, 3 – thermal effect of water freezing, 4 – heating at a heating rate of 20 K min^{-1}, 5 – thermal effect of ice melting

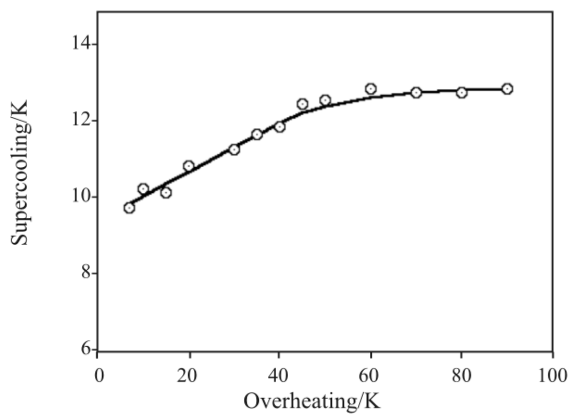

Fig. 2 Dependence of water supercooling on overheating temperature

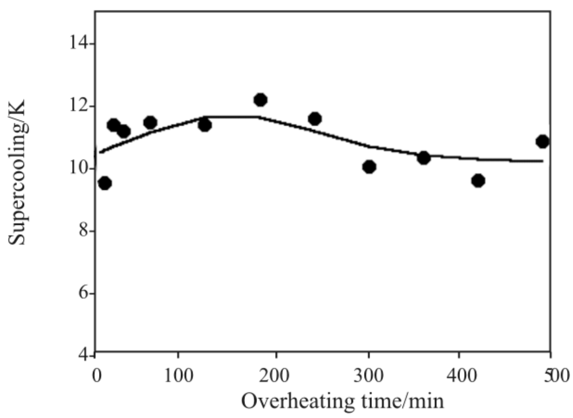

Fig. 3 Dependence of water supercooling on overheating time

slightly decreased to about 10 K and certain fluctuations in a temperature range of about 0.5 K occurred. In the measurements at longer overheating times the supercooling can be influenced by degassing of water due to long-term heating at high temperatures.

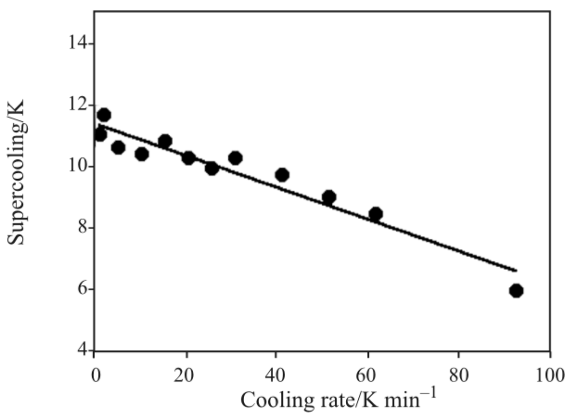

Fig. 4 Dependence of water supercooling on cooling rate

The dependence of the degree of water supercooling on cooling rate at a constant overheating temperature of 25°C and holding time of 30 min is shown in Fig. 4. The water supercooling decreased with cooling rate. While at the lowest rates the supercooling was found in a range between 11 and 12 K at a cooling rate of 90 K min^{-1} it only reached 6 K.

The found degrees of supercooling and their changes are low although water was thermally treated in broad range of overheating temperatures and times and cooling rates. Only cooling rate may have a greater effect on the water supercooling than overheating time and temperature. It seems that water supercooling is only limited influenced by thermal treatment and the heterogeneous nucleation is a prevailing process determining start of water freezing in our experimental arrangement. Finding conditions of thermal treatment that activaly influence the degree of water supercooling and water freezing persist a challenge.

Conclusions

Water supercooling was determined by methods of thermal analysis by a direct temperature measurement in a water droplet depending on various overheating temperatures and times and cooling rates. Applied thermal treatment influenced degree of water supercooling but only to a certain extent. Water supercooling increased slightly with temperature and time of overheating and decreased with cooling rate. Maximum found value of supercooling was 13 K reached at a cooling rate of 1 K min^{-1}, overheating time and temperature were 30 min and 25°C, respectively. The greatest change in supercooling of 6 K was determined when cooling rate was decreased from 90 to 1 K min^{-1}. In the overheating temperature range in question supercooling only varied in a range of 3 K.

Small degrees of water supercooling and their changes with thermal treatment indicate that heterogeneous nucleation is a prevailing process determining start of water freezing in our experimental arrangement. The supercooling and its changes depend more on properties of contact surface than on previous thermal treatment. It was shown by our pilot experiments when the supercooling found on an Al foil was 4 K, while on a quartz plate between 10 and 13 K and on a silicone surface practically 18 K. By small influence of thermal treatment on its supercooling water differs from molten salts in which previous thermal treatment was crucial for their supercooling [11].

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