Journal of Electron Devices, Vol. 4, 2006, pp. 97-100

© JED [ISSN: 1682 -3427]

Journal of Electron Devices

Thermal and dynamic study of water crystallization at the supercooling breakdown

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Abstract

Through temperature measurements, an experimental study has been carried in order to examine the thermal phenomenon at supercooling breakdown, but also to study the crystallization kinetics. Photographic pictures have been made to observe the solid-liquid interface.
Key words: Supercooling; supercooling breakdown; crystallization thermal effects; ice dendrites; crystal growth.

1 Introduction

In the environmental reduction impact context of fluids industrially used for refrigerating production, the alternative technology (indirect production of cold) using a secondary fluid permits to dissociate the production function from the distribution function. The production unit is then more compact. The fluid mass involved is minimized and, moreover, its containment is improved. Among the possible secondary fluids, two-phase refrigerants (called ice slurries) constitute a promising solution. They are presented as a two-phase mixture in which the solid phase is water in fine ice particles (whose latent heat of fusion is approximately 335 KJ.kg-1) while the carrying liquid phase is generally a binary aqueous solution.

Currently, the expansion of the ice slurries uses is related to the development of machines able to produce them in a
continuous, reliable and effective way from an energy point of view. Several methods of production are being studied, among which ice slurry production from supercooled water crystallization [1].

The study presented hereafter is in this context and permit to obtain dynamic and thermal informations of supercooled liquids crystallisation. The material used within the framework of this study is water.

1.1 Supercooling

Supercooling is the state of a material which remains in liquid phase whereas its temperature is lower than its melting temperature. It is a state known as metastable, i.e. it can evolve to a steady equilibrium state after a disturbance of sufficient intensity.

The supercooling degree is defined by ΔT as being the difference between the melting temperature T_f and the temperature at which the crystallization is initiated T_c :

$$\Delta T = T_f - T_c > 0$$

The supercooling degree may be affected by various parameters [2, 3]:

- sample volume (it is the most important parameter influencing ΔT : the lower volume of the liquid is, the more the supercooling is important) ;
- cooling rate ;
- pressure ;
- concentration in case of binary mixtures.

In case of supercooling, a sufficient disturbance starts the fast transition towards the solid state and the metastable state ceases (supercooling breakdown).

1.2 Supercooling breakdown

When the transition begins abruptly, the liquid changes to the solid state and takes a ramified form. To highlight this phenomenon, we visualize this growth using a video equipment allowing to take several pictures rapidly (110 pictures/s).

On figures 1, 2 and 3, we can see that the solid front progresses by forming a dendritic structure composed of solid branches growing in a preferential direction. The medium is then diphasic. Different tests indicate that the growth rate of these ice branches is conditioned by the supercooling degree: the more important the supercooling degree is, the faster the dendrites growth rate is.

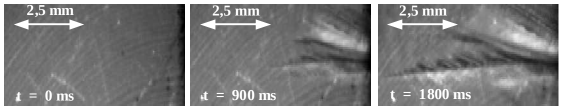

FIG. 1, 2 & 3 – *Visualization of the dendritic progress in a supercooleed water ($\Delta T = 2.1K$)*

This structure is the consequence of a solid growth in an unstable liquid medium. This phenomenon is more known under the name of “instability of Mullins-Sekerka”: when a solid is in a supercooled liquid, it grows following a process of dendritic formation [4].

Let us recall that the medium is diphasic during this solidification period. The fields where the ramifications appear are zones which broke the supercooling locally but leaving the close zones liquid.

Crystal progress by supercooling breakdown is accompanied by a characteristic release of heat (the latent heat of crystallization). Supercooling breakdown is detected by an increase of temperature from the crystallization temperature T_c generally to the melting temperature T_f , as shown in the figure 4.

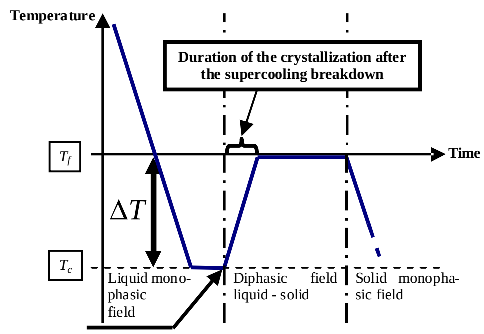

FIG. 4 – *Change of the temperature of the liquid sample during its cooling to a stage of temperature T_c followed by its solidification after disturbance of the system.*

During the increase of the temperature, dendrites develop along preferential directions with a rate dependant on the degree of supercooling. An experimental study has been implemented in order to examine this aspect of the phenomenon.

2 Experimental technique

In order to impose the crystallization direction, we chose to study the crystal progress within a capillary tube.

The experimental device reproduced in figure 5 is composed of three parts.

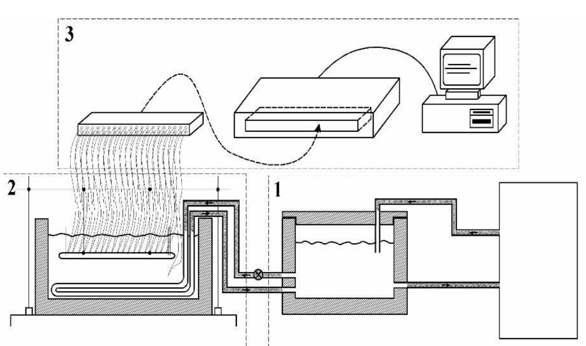

FIG. 5 – *Experimental device intended to visualize thermically the crystal growth by supercooling breakdown.*

Part 1 sets up the chiller allowing to cool the refrigerant fluid. Part 2 is the cooling tank. The refrigerant fluid from the chiller flows to the cooling tank through an exchanger. The test cell is submerged into a water ethanol mixture cooled down by the exchanger. Part 3 represents the temperatures acquisition unit. It has a fast acquisition board on which twenty thermocouples can be connected. This acquisition unit is linked to a computer for the treatment and the storage of measurement data.

The instrumented cell is a 25 cm length capillary copper tube, having an internal diameter of 2.4 mm. Several reasons led us to make this choice, in addition to channel the crystal progress. First of all, low volume of water authorizes important supercooling degrees [2, 3]. The access to a wide range of supercooling degrees enables us to study their influence on the dynamics of crystal growth. Copper was adopted for its facilities of machining, its rigidity and to permit a relatively fast cooling.

On the internal wall of the tube, 19 thermocouples (T_i , $i \in [1;19]$) of K type, 0.2 mm in diameter, are laid out and distributed in an all the more dense way as they are close to the zone of germination (see figure 6). These thermocouples are adapted for measurements at low temperatures. They present a very short response time (approximately 50 ms) and a correct accuracy about 0.1 K. They are fixed using a thermofusible adhesive (polymeric EVA) of low conductivity (approximately 0.2 W/m.K).

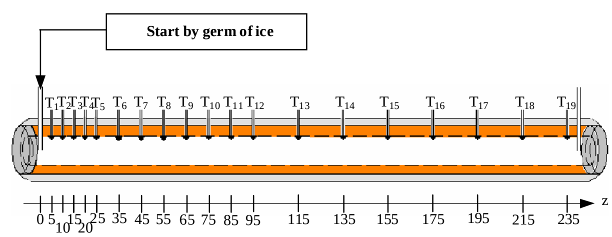

FIG. 6 – *Position (in mm) of the 19 thermocouples in the test cell.*

The tube is cooled until the liquid reaches a low temperature at any point of the field. When the temperature is stabilized, we cause the supercooling breakdown by a seeding, using an ice germ introduced at the extremity of the tube. This germination point constitutes the initial position of the solid front (z = 0 mm). In this manner, the intensity of the supercooling, the moment of its breakdown, and its localization are controlled.

The data acquisition unit is configured to take the temperatures field every 75 ms. The acquisition starts no long before the seeding.

3 Results

Tests have been carried out with the bath temperature maintained at different supercooling breakdown temperatures. They correspond to crystal growths initiated with various degrees of supercooling. The results presented below are two examples of tests, the first with $\Delta T = 1.6K$, the second with $\Delta T = 5.1K$ (see figures 7 and 8). The legends correspond to the z-coordinates of the thermocouples along the capillary, as they are schematized in figure 6.

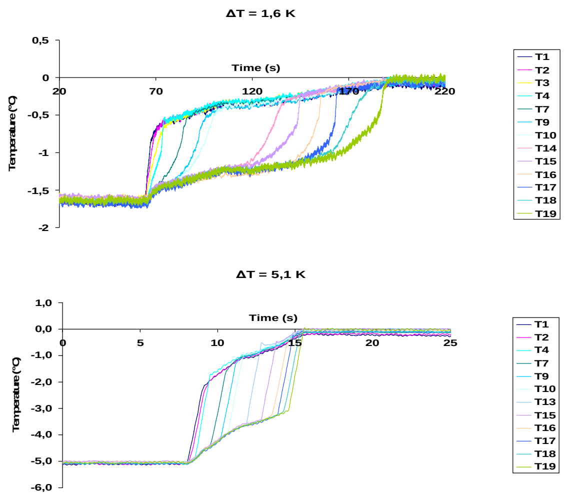

FIG. 7 & 8 – *Two examples of supercooling breakdown.*

It is noted that, whatever the supercooling degree, the temperature increase after the seeding is the same in all the tests. The thermocouples close to the starter zone indicate a sudden increase, followed by a slower evolution towards the melting temperature. On the contrary, the more distant thermocouples indicate a slow increase, followed by a faster evolution towards the melting temperature.

The sharp rise in the starter zone is due to a quasi-instantaneous formation of ice. At the first points, the temperature does not reach the melting temperature ($T_f = 0°C$). On the other hand, the more distant thermocouples show, at the beginning, a slow increase of the temperature, due mainly to conductive effects in copper. The ice front crossing in the channel central zone is characterized by the sharp increase in temperature.

We note that the larger the degree of supercooling is, the shorter the time for the dendritic front crosses all the capillary tube length is. Each thermocouple allows to determine the instant when the dendritic front pass. Knowing their position, we can then represent the distance covered by the ice front according to time (see figures 9 and 10):

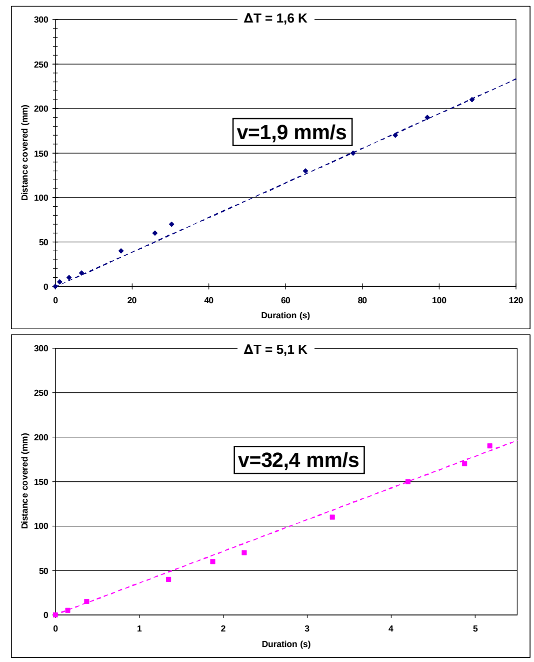

FIG. 9 & 10 – *Representation of the distance covered by the front according to time.*

We observe a linear dependence of the front position with time. So the growth rate v is deduced by the slope of these curves which show that the rate is practically constant during all the ice progress.

Supercooling degree	*Growth rate v*	*Accuracy*
K	*mm.s^{-1}*	*mm.s^{-1}*
1.2	1.2	-
1.6	1.9	-
1.9	3.4	-
2.7	5.5	0.1
3.2	7.8	0.1
3.7	12.3	0.2
4.1	17.0	0.3
4.4	20.7	0.7
5.1	32.4	0.9

TABLE 1 – *Propagation velocity of the ice front for various supercooling degrees.*

Figure 11 indicates that the velocity is increasing with the supercooling degree. On the contrary, when the supercooling degree becomes very weak, this rate tends towards zero. A power law versus the supercooling degree ΔT can be established:

$$v = 0{,}51.\Delta T^{2{,}52} \quad (v \text{ in mm/s})$$

The form of this crystal progress law is not new. At the end of the Seventies, American researchers had tried to establish a power type law [5]. More recently, Japanese researchers established the same law type [6, 7]. But their kinetics laws apply only to the zone close to the site of germination, in other words where starts the dendritic front, and not to longer distances as the study shows it here. Here, the study is founded on thermal effects of dendritic growth and permits to give a law of its kinetics.

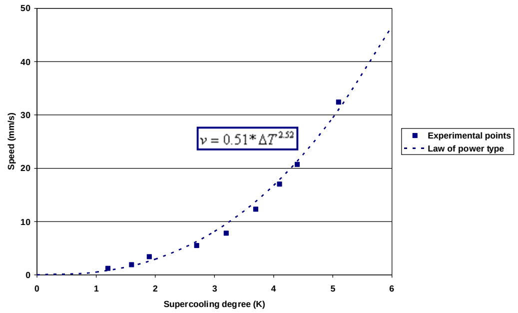

FIG. 11 – *Experimental rate of the dendritic front according to the degree of supercooling (case of water).*

4 Conclusion

This article presents the research work advancements about crystallization. It presents phenomenological descriptions of crystal growth by supercooling breakdown. This article proposes also to present an experimental method which determines the crystal propagation rate by temperatures statements and to establish a kinetic law, which opens prospects as for the use of this same technique applied to other materials, in particular diphasic refrigerant fluids.

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