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Crystallization and recrystallization of quick-frozen salmon sprayed with dry ice were investigated

Bin Fang [1], Xinrong Zhang [2]

[1] School of Shanghai Maritime University, Shang Hai, China;

[2] School of PeKing University, BeiJing, China.

Abstract

Frozen salmon is an important way to transport and store salmon. The freeze-thaw damage and biochemical decay of salmon are closely related to ice crystals. this paper through experiment contrast salmon spray freezing and refrigerator freezing explore the salmon freeze way and the size of ice crystal and recrystallization, compared with dry ice spray freeze, natural convection freezing, impingement freeze calculation data, it is concluded that the dry ice spray can in a way that is gas at low temperature and sublimation phase change of frozen salmon, can also weaken the boundary layer thickness, cooling effect is better than that of the impactor under same conditions of freezing and liquid nitrogen spray freezing conclusions; Also, some problems about ice crystal growth and recrystallization were also explored. Recrystallization will increase the size of ice crystals, so the damage caused by recrystallization may be more serious than the damage caused by salmon cells during the initial freezing.

Keywords

Crystallization and recrystallization, dry ice.

1. Introduction

Salmon enjoys the reputation of "treasure in water". Salmon has small scales and few spines in appearance. Its meat color is bright red, rich in a variety of unsaturated fatty acids, and fresh and tender in quality. China is a big demand for salmon, 5% ~ 6% a year growth, salmon in China market, the frozen salmon market is relatively stable, but the ice fresh market growth is very blocked, the main reason is that the consumer demand for fresh salmon has a relatively large, but at present, China's domestic salmon, for the most part, are all from the dimension higher global salmon farming base, Chile, Norway, ice fresh salmon can guarantee the salmon but for cold-chain fresh demand is higher, need short shipping time; The frozen salmon can be kept for a long time and has low requirements on the cold chain, but the quality of the frozen salmon is greatly reduced after rewarming, which cannot meet the demand of consumers for fresh salmon [1]. Therefore, there is an urgent need to find a way to preserve the quality of salmon freezing.

The effect of frozen salmon on salmon quality can be divided into two parts.

The temperature of salmon decreases in the freezing process, and the salmon meat is frozen. In the freezing process, the biochemical reaction changes inside the meat have little influence on the quality, mainly due to the changes in physical properties, because the meat freezes for a short time and at a low temperature. During freezing, the cells inside the fish are filled with ice crystals. In the cooling process, due to some molecular thermal physical properties and characteristics of the meat temperature gradient, ice crystals are widely distributed near the cell membrane, intracellular ice crystals with some sites on the cell membrane as the crystal nucleus [2], ice crystals started on the cell membrane for the center with crystal nucleus growth, pure water when the ice volume increase 9% [3], this leads to the cell under the influence of ice

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crystal growth stress, cell membrane prone to burst; Also, proteins in cells are affected by the growth stress of ice crystals during freezing, and the spatial structure of proteins is deformed or even the polypeptide chain is broken, leading to protein denaturation.

frozen salmon in the process of transportation and storage is relatively stable, but the growth of intracellular ice crystals spontaneously, this is the recrystallization phenomenon [4], recrystallization phenomenon is generally recognized as a part of the growth of ice crystals rearrange the spontaneous phenomenon, recrystallization phenomenon causes ice crystals size increases, recrystallization phenomenon is greatly influenced by the temperature, the lower the temperature of recrystallization phenomenon is not obvious, about high temperature or temperature fluctuations, the greater the recrystallization phenomenon more obvious, ice crystal size will be bigger [5]. Salmon is rich in unsaturated fatty acids, other frozen unsaturated fatty acids react with oxygen in the air after the lipid oxidation product of promoting protein denaturation [6], another due to large crystal size effects on the cell membrane, the influence of cooling when the temperature gradient, the lysosome membrane inside the cell is more vulnerable to the destruction of the ice crystals, lysosome membrane rupture after can lead to a large number of enzymes into the cells, the resulting more complicated and serious cell damage [7, 8].

The fundamental reason for the low quality of frozen salmon is that the characteristics of salmon are changed by the formation of ice crystals by water in the meat during the process of refreezing. Therefore, to improve the frozen quality of salmon and reduce the influence of ice crystals on cells, the size of ice crystals should be reduced during freezing [9, 10].

People tend to use more direct contact cooling, air blast refrigeration, immersion cooling, spray methods of refrigeration, the refrigeration method can achieve large quantities of frozen, but the ice crystal size is opposite bigger, a relatively large effect on meat quality, and more with freon as refrigerant, easy to cause abnormal ozone depletion, climate change, acid rain, and another bad phenomenon. Carbon dioxide gas as a kind of environment, nonpoisonous and harmless, can be in contact with the food, in an atmospheric pressure environment for carbon dioxide or dry ice, good performance of cooling and cleaning, dry ice as a solid carbon dioxide has itself has good capability of heat absorption, and carbon dioxide for non-polar molecules, better surface from intermiscibility, people often use carbon dioxide gas in the high-pressure cleaning tools, high-speed dry ice particles on the surface of the rapid evaporation at the same time can instantly dismember stains [11], dry ice as a new type of cooling medium can effectively by quickly reduce the temperature of frozen fish, Also, CO2 from dry ice has a certain antibacterial effect [12]. However, few studies use dry ice as a refrigerant to spray quick-frozen food. Therefore, this paper takes dry ice spray quick-frozen salmon as a study to explore the influence of carbon dioxide solid-gas spray on the crystallization of salmon.

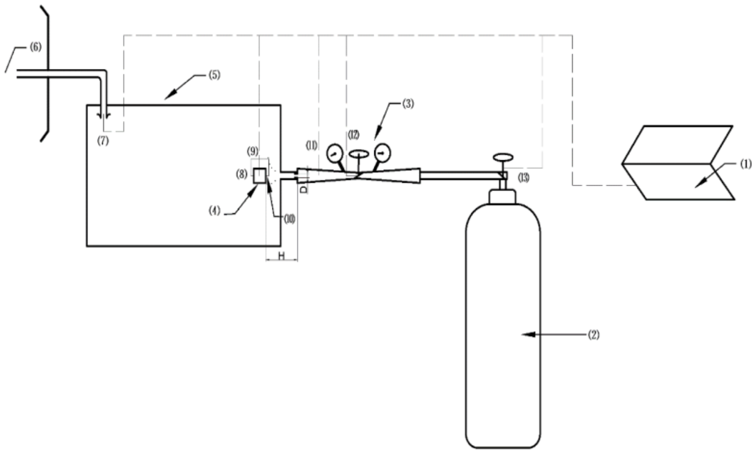
2. Materials and devices

2.1. Materials and instruments

Fresh salmon, weighing 300~1000g and with a body length of 25~40cm, are purchased from Jinxiu Dadi Wholesale Market, Haidian District, Beijing.BC/BD-100HER Haier Freezers Jingdong Haier Jinqiao Store;SH-700 Multichannel Data Recorder Shenzhen Shenhuaxuan Technology Co., Ltd.KD201a Pathological Slicing Machine, Jinhua Kedi, Zhejiang;EB-38BDI MacDior Microscope Xiamen MacAudi Industrial Co., Ltd.

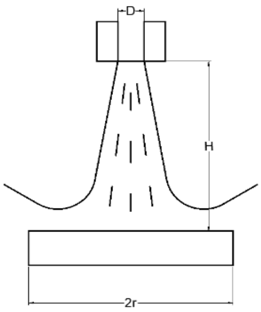
2.2. Experimental device

The dry ice spray quick-freezing device used in the experiment is shown in Figure 1, which is mainly composed of a liquid carbon dioxide high-pressure cylinder, carbon dioxide step-down valve, PMMA box body, and computer. Its working process is meat to be included in the box, and then open the carbon dioxide high-pressure cylinder, then open the decompression valve, liquid carbon dioxide vaporizing occur, and evaporation absorbs a lot of heat the surrounding gas in low-temperature solidification, the resulting a large number of low-temperature gas and dry ice, cold gas and dry ice heat exchange with the meat quickly, meat is frozen.



(1): Computer ,(2) Co2 cylinder, (3): Decompression valve, (4):meat, (5):PMMA box, (6):Outdoor pipe, (7-11):thermocouple, (12-13):Solenoid control valve

Fig. 1 : CO_2 spray quick-freezing device



Nozzle diameter:D= 6mm, Meat block length:r=15mm

The length of the nozzle from the meat:H=65mm

Figure 2: A partial enlargement of a meat block sprayed by a nozzle

2.3. Experimental methods and results

Put the fresh salmon bag into a certain amount of carbon dioxide, salmon is suffocated, wash and clean up at the side of the salmon to take out the meat, fish skin effect on heat transfer bigger [13], so meat peel and trim the cube into 3 * 3 * 1 cm3, will meat sample label and divided into three groups, each group of three sample pieces to repeat the experiment to reduce the error. The first group was treated as a blank control group without treatment. In the second group, thermocouples were inserted into the front, middle and back parts of the fish blocks, and then the fish blocks were placed in a PMMA box to start the dry ice spray device. After the fish blocks were quickly frozen to the central temperature of -18°C, the fish blocks were taken out, and the frozen fish slices were sliced to 0.5mm, and the reheating process of the fish blocks at 20°C was observed under a microscope.

In the third group, a thermocouple was inserted into the front, middle and rear parts of the fish blocks, and the lowest temperature of the freezer was set at -30°C. After the freezer temperature was completely reduced to the lowest temperature, the fish blocks were put into the freezer, and the central temperature of the fish blocks was frozen to -18°C. The fish blocks were removed and quickly sliced and placed under a microscope.

2.3.1 Calculation energy of frozen fish

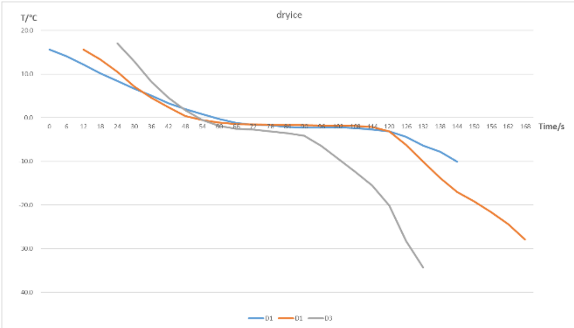


Fig. 3 Cooling curve of dry ice spray fish

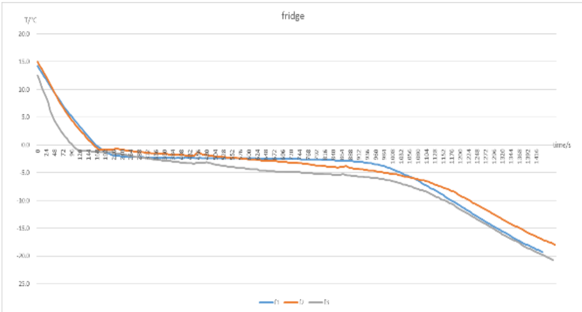


Fig. 4 Freezing and cooling curve of the refrigerator

In the dry ice spray quick-freezing experiment, the carbon dioxide nozzles of D1 and D2 samples were blocked, which led to the prolonged freezing time of D1 and D2 samples. However, no clogging occurred in the spray process of D3 samples, and the cooling curve of the samples was relatively flat in the solidification stage, so the experimental data of D3 was selected. In the refrigerator quick-freezing experiment, sample F3 with a relatively gentle cooling curve in the freezing process was selected as the experimental data.

Table1 : Salmon date

	ω %	m (g)	λ ($w/m \cdot k$)	c ($kj/kg \cdot k$)	q_0 (kj/kg)
Value	72.51	9.63	0.4711	3.5894	334

The heat absorbed by salmon in freezing is mainly composed of latent heat of freezing water inside the meat and sensible heat of cooling[14, 15].

$$Q_{潜} = m\omega q_0 \quad (1)$$

$$Q_{显} = cm\,(T_1 - T_2) \quad (2)$$

$$Q_{总} = Q_{显} + Q_{潜} \quad (3)$$

Table2 : frozen salmon date

	Fridge	Dry ice
T1	-0.2	-0.5
T2	-3.8	-6.5
T3	-2	-3.5
T4	-27.25	-60
t	792s	42s

The initial temperature of the frozen fish : T1

The final temperature of the frozen fish : T2

The average temperature of the frozen fish : T3

The environment temperature : T4

Time : t

2.3.2 Convective heat transfer coefficient

Heat flow density :

$$q = \frac{Q_{总}}{\tau} \tag{4}$$

$$q = \frac{\Delta T}{R} \tag{5}$$

The total thermal resistance:

$$R = \frac{1}{Ah_1} + \frac{\delta}{2A\lambda} \tag{6}$$

For the calculation of the convective heat transfer coefficient of impinging jet, the geometric parameters are shown in Fig. 2. The quick freezing of 19m/s is the same as that of dry ice spraying.

$$2\times10^3 \leqslant \mathrm{Re}_D \leqslant 4\times10^5 \qquad 2\leqslant \frac{H}{D} \leqslant 12 \qquad 2.5\leqslant \frac{r}{D} \leqslant 7.5$$

$$(Nu_D)_m = 2\mathrm{Re}_D^{0.5} Pr^{0.42}(1+0.005\mathrm{Re}_D^{0.55})^{0.5} \frac{1-1.1D/r}{1+0.1(H/D-6)D/r} \frac{D}{r} \tag{7}$$

$$Nu_D = \frac{h_r D}{\lambda} \tag{8}$$

$$\mathrm{Re} = \frac{u_e D}{\nu} \tag{9}$$

2.3.3 Boundary Layer Calculation Formula

$$\delta = \frac{5x}{\sqrt{\mathrm{Re}_x}} \tag{11}$$

$$\frac{\delta}{\delta_t} \approx Pr^{1/3} \tag{11}$$

2.4. Calculation Results

The solid-gas ratio of dry ice spray is 1:1, the cooling capacity is 2:1, the total rate is 19m/s, the dry ice flow rate is 2.08g/s.

Table3 : Heat transfer date

	Fridge	Dry ice	Air blaster
h	45.07	643． 83	199.32
Re	Natural convection	1.556×10^5	96670
Flow boundary layer		1.389xe-5m	1.98xe-4m
Thermal boundary layer		1.56e-5m	2.22e-4m

3. Analysis and discussion

3.1. Analysis of calculation results

Accounted for most of the nitrogen content in the air, Pr number can be used as a kind of momentum diffusion and heat diffusion ability of one dimension, and 60 ° C n2 and co2 Prandtl number are less than 1, so the momentum diffusion capacity is small, so a lot of engineering by forced convection means to enhance the heat transfer, the large temperature difference is, of course, the convective heat transfer coefficient of impingement is greater than the refrigerator natural convection for another reason.

In the process of dry ice spray freezing, due to the small space in the nozzle, large pressure difference, and rapid vaporization of liquid CO2, it is considered that the process is an isentropic adiabatic process. As a result, the cooling capacity generated by mass vaporization makes CO2 gas rapidly condense into dry ice particles, which are about 1um-0.1mm[16, 17]. The ratio of dry ice to CO2 gas is about 1:1 [18], and the cooling capacity of dry ice and CO2 for salmon is about 2:1.

The boundary layer of the experience formula of the calculation is more complicated so the estimate to understand the effects of dry ice on the heat transfer boundary layer, the calculation result, spray dry ice boundary layer to 7%, the convective heat transfer coefficient of liquid nitrogen spray for 425 [19], conveyor belt, the heat transfer coefficient of liquid nitrogen to 170 [20], the phase transition temperature of liquid nitrogen is much lower than that of liquid co2, n2 and co2 pr number average is about 0.7, maybe just due to liquid nitrogen spray cryogenic nitrogen gas, cryogenic gas or - solid heat transfer, rely mainly on the sensible heat of the nitrogen to absorb heat. Liquid CO2 spray is solid gas-solid heat transfer, and the sublimation rate of dry ice will increase with the increase of the temperature of the solid wall, or with the decrease of particle size [21]. Dry ice can be hit on salmon pieces in close contact with phase change and absorb heat, and the low-temperature CO2 gas generated by phase change can absorb heat again [22]. Dry ice sublimation nearly 400 times the volume expansion, on the one hand, can be generated in the fish surface of the larger disturbance weaken the boundary layer (23, 24), on the other hand, after the dry ice sublimation dry ice can continue to play behind the sublimation heat absorption on the salmon pieces, this means that by adding just 2 g/s dry ice particles through the cold cuts in the boundary layer, with phase change sublimation to learn salmon phase change heat, so will greatly improve the heat transfer rate, under the cooling rate of the fast enough quick in intracellular solution crystallization temperature area can greatly decrease the size of ice crystals, even become a glassy state (0) ice crystal size [19].

3.2. Analysis of cooling curve

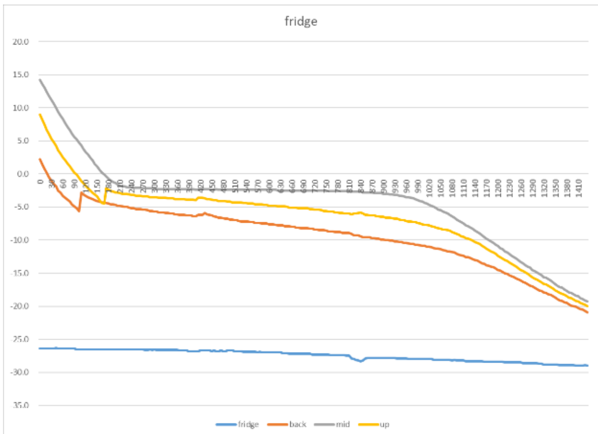


Fig. 5 Shows the cooling curve of the F3 sample

The fridge is the cooling curve of the frozen environment, the back is the thermocouple at the bottom of the meat, the mid is the thermocouple at the center of the meat, and up is the thermocouple at the top of the meat.

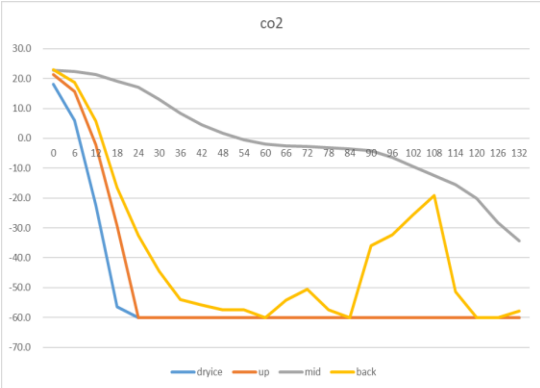


Figure 6 : Samples for d3 cooling curve

Where Dry ice is the cooling curve of the freezing environment, Back is the thermocouple at the back of the meat to the spout, Mid is the thermocouple at the center of the meat, and Up is the thermocouple at the meat to the spout.

In Figure 5, the backline and up line have certain temperature fluctuations at 100s and 160s respectively, while the midline is relatively flat. According to Figure 5 and 6, the freezing point of salmon meat is about -0.7°C, while the thermocouple temperature at back and up in Figure 5 is about -5°C, which is because there is a certain degree of supercooling in the freezing process of meat [25]. Back and up the thermocouple to meat and exposed in the refrigerator, maybe due to the pieces on both sides of the cell nucleus and less because of the cooling rate is opposite bigger, the water molecule is not easy to be captured with a crystal nucleus when the pieces on both sides to about 5 ° C too cold, nucleation number increased, the pieces on both sides of the rapid solidification and phase change heat release, on both sides of the low-temperature environment is not enough to draw the phase change heat, result in higher temperature, and mid thermocouple temperature fluctuations may be due to pieces not occurring in the middle of the freezing rate is lower than the pieces on both sides, water molecules more easily to be captured in crystal nucleus from this center slow freezing no supercooling phenomenon happens.

As shown in Figure 6, the large temperature fluctuation at the back from 84s to 114s was mainly due to the blocking of the nozzle, which led to a slight rise in the temperature at the back. As the meat was at -60°C ambient temperature, the cooling rate of the meat was great, the number of crystal nuclei was large and the solidification heat could be taken away in time, so the temperature fluctuation was caused by supercooling did not appear in Figure 6.

3.3. The crystallization

Figure 7-1 and 7-2 show the fish blocks after dry ice spray freezing and rewarming, while Figure 7-3 and 7-4 show the meat blocks after refrigerator freezing and rewarming.

In the process of frozen meat, because the cell temperature is reduced, liquid solubility in the cell changes, part of the water precipitation freeze into ice crystals, while the slower cooling rate of the more precipitation water ice crystal size, the greater the [6], so the frozen meat after thawing will produce certain moisture content, the process is almost irreversible, and precipitation water the more the greater the damage of cells (26, 27).In cooling water into ice mainly for liquid crystal nucleus is generated in the process of the then or hydrated molecules of water molecules in the crystal nucleus gathered near the formation of ice crystals [27], in a certain volume of liquid, the number of crystal nucleus largely determines the size of the ice crystals, because we are unable to add material in the cell, general intervention by increasing physical fields or a cooling way to increase the number of crystal nucleus, temperature lowering can reduce nucleation conditions; Once, drop in the number of crystal nucleus dating to 50 times, because the ice crystals are tetrahedral structure, we can assume that ice crystals are crystal nucleus at the center of a sphere, each drop can be roughly calculated once the size of the ice crystals will shrink by 86%, so in general the cooling process of the lower the temperature, the smaller the size of the ice crystals.

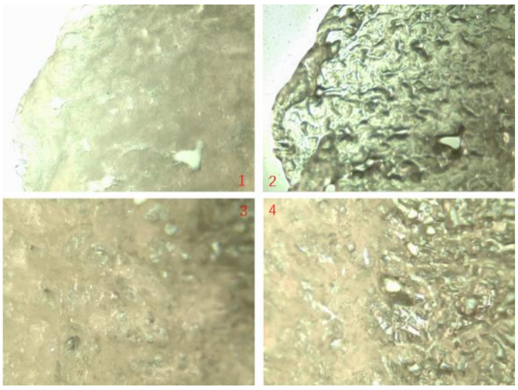


Figure 7 : Crystallization of salmon

The fillets after temperature environment are 23 ° C temperature environment, compared to 7-1, 7-3 figure can be seen that dry ice spray freeze ice crystal size is less than the refrigerator to freeze, and figure 7-1 ice crystals distribution more uniform, tiny ice crystals evenly mean cells are frozen irreversible damage under the condition of low [16], contrast figure 7-2, 7-4 shows relatively close, the arrangement of the cell and figure 7-4 piece cells can be observed due to ice crystals extrusion, intercellular space is larger, after thawing clearance by ice into water, precipitation and surface water than figure 7-2, after observing the frozen meat thawing process, Large ice crystals of meat will be more visible water flow phenomenon.

3.4. Recrystallization problem

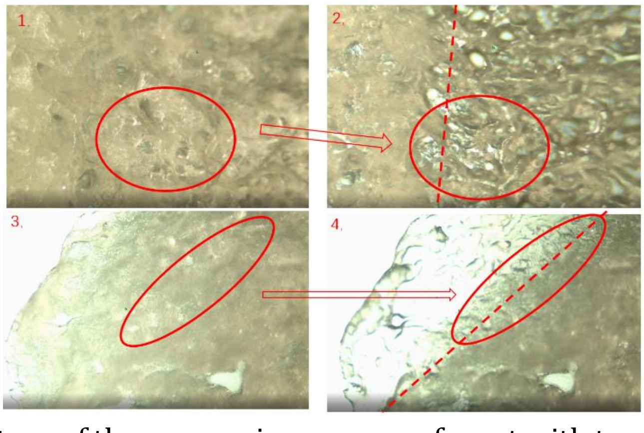


Fig. 8 :shows the picture of the rewarming process of meat with two freezing methods.8-1and8-2 are for refrigerator freezing, and 8-3 and 8-4 are for dry ice spray freezing. In Figure 8-2, the left side of the dotted line is in the frozen state and the right side is in the melted state. In Figure 8-4, the left side is in the melted state and the right side is in the frozen state.

Observe the picture is large than small ice crystals on the surface of ice crystal surface is more clear and transparent, small ice crystals surface will be fuzzy, close to the frosted glass surfaces, respectively, compared to 8-1, 2 and 8-8-3, 8-4 same position can see a dotted line near the ice crystals size increases slightly, which means that the recrystallization phenomenon will appear in the process of thawing, recrystallization as a spontaneous phenomenon of food quality is greatly bad [1], the cells in the thawing process will be affected by the secondary damage of ice crystals, and because the recrystallization leads to the original size of ice crystals generated larger ice crystals (26, 28), Since the time of rewarming is far less than that of freezing, the extent of damage to cells caused by recrystallization during rewarming remains to be determined.

Both crystallization and recrystallization phenomenon for salmon cell damage is indisputable, and the crystallization and recrystallization phenomenon is in 0 ° ~ 5 ° C - C the largest ice crystal formation zone [3], both in freezing and thawing should make the food in the temperature range takes as short as possible, of course, the freezing process and as much as possible to increase the number of crystal nucleus.

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