Crystallization process and Nucleation Kinetics of Mg²⁺//SO₄²⁻, NO₃⁻·H₂O system
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ABSTRACT
In order to achieve efficient recovery of ions from the simultaneous desulfurization and denitriﬁcation wastewater, the effects of various factors (i.e. the saturation temperature, the cooling termination temperature, the stirring rate and the cooling rate) on crystallization yield, metastable zone width and crystal morphology were investigated to determine the optimal crystallization conditions of Mg²⁺//SO₄²⁻, NO₃⁻·H₂O system. According to the results of experiments, the nucleation kinetics were also speculated by Nyvlt self-consistent equation and classical 3D nucleation theory. Also, the crystallization products were characterized by X-ray diffraction and scanning electron microscopy. Under the determined optimal conditions, the yield of the crystal can reach 78%, and the crystal products were veriﬁed as pure MgSO₄ 7H₂O, whose morphology is complete without defects.

Key words | crystal morphology, crystallization yield, metastable zone width, MgSO₄, nucleation kinetics

INTRODUCTION
The flue gas emissions of small-sized or medium-sized industrial boilers, which are the second major source of pollution represented by steel, cement and glass industries in China, have not been effectively controlled yet. However, the mature technologies of sulfur dioxide (SO₂) and nitrogen oxides (NOx) removal in power station boilers cannot operate efﬁciently and steadily in industrial boilers. Therefore, our group has developed a simultaneous desulfurization and denitriﬁcation technology based on the magnesium oxide (MgO) method (Zhao 2014; Li et al. 2019), which has many advantages; that is, high desulfurization and denitriﬁcation efﬁciencies, low investment and operation cost, simple maintenance and operation, strong adaptability to coal types, and safe operation. However, there are a great number of ions in the desulfurization and denitriﬁcation wastewater, such as chlorine ions (Cl⁻), sulfate ions (SO₄²⁻), nitrate ions (NO₃⁻) and magnesium ions (Mg²⁺). If wastewater is directly discharged into the environment, it will result in serious secondary pollution and resource waste, which has become the bottleneck in the development of this technology. The wastewater treatment methods commonly used include the discarding method, double alkali method (in which the by-product is gypsum), and evaporation crystallization recovery method. These methods have the problems of large amounts of by-products, occupying land, and low product quality (Yan et al. 2018). Hence a cooling crystallization process with optimized operating conditions is proposed to recover magnesium salt from the simultaneous desulfurization and denitriﬁcation wastewater in our study. The recovered magnesium salt can be used as a kind of raw material for magnesium fertilizer and magnesium-based building materials with a high application value and a large market demand, which greatly promotes the enthusiasm of enterprises for desulfurization, denitriﬁcation and wastewater recovery.

As a kind of technology for separating and purifying chemical products in the chemical industry, the main purpose of crystallization technology is to obtain crystals with high purity, uniform particle size, and complete morphology.
(Jiang et al. 2015). The key to achieving this goal is to optimize and control the metastable zone width (MSZW) during the crystallization (Pritula & Sangwal 2015; Wang et al. 2016). MSZW is affected by the characteristics of crystallization solution (such as the initial concentration of the solute, stirring rate, cooling rate, and cooling termination temperature); meanwhile, the influence law would vary completely with different systems. In addition, it is necessary to investigate the crystal nucleation kinetics in order to search out the changing law of MSZW and its dependence on various factors. However, the factors causing nucleation are complicated. At first, Nývlt (Nývlt & Mullin 1970) assumed that the maximum supersaturation was proportional to the maximum supercooling, but the physical meaning of the parameters in the equation was unclear. Subsequently, Sangwal et al. (Sangwal & Wojcik 2009; Kadam et al. 2012; Shiau 2016) proposed the classical 3D nucleation theory and studied the effects of impurities such as iron ion (Fe$^{3+}$) and SO$_4^{2-}$ on the nucleation kinetics of phosphoric acid (H$_3$PO$_4$) system. It was found that impurities such as Fe$^{3+}$ and SO$_4^{2-}$ decreased the kinetic coefficient and increased the MSZW to different extents, and the decrease of the adsorption heat value in thermodynamics also proved that the presence of impurities inhibited nucleation, indicating that the kinetics of different systems were different. Himawan et al. (Himawan et al. 2006) carried out a study on the recovery of purified magnesium sulfate heptahydrate (MgSO$_4$·7H$_2$O) crystals from a magnesium sulfate industrial stream emitted from flue gas desulphurization. It was found that MgSO$_4$·7H$_2$O occurred during the subsequent filtration and drying above 0.4 °C, which was rather needle-like. The recovery of magnesium sulfate from low-grade ascharite was also researched, and the recovery rate of MgSO$_4$ reached 45.03% under the obtained optimum conditions (Li et al. 2016). But MSZW was not mentioned in the paper. Zhang et al. (Zhang et al. 2019) investigated the influence factors of MSZW and nucleation. The results showed that different growth rates in the same system led to differences in crystal morphology. The crystal morphology of magnesium sulfate heptahydrate (MgSO$_4$·7H$_2$O) tended to be acicular with the increase of supersaturation. And the main factor affecting nucleation and growth parameters was supercooling.

The above research results have made great contributions to the development of cooling crystallization technology and theory. At the same time, they also verified that the factors affecting the crystal composition and morphology, MSZW, nucleation order and solid-liquid interface energy, as well as their influence laws, were closely related to the characteristics of the research system. Even systems with similar properties may show completely different crystallization characteristics due to different operating conditions or ion composition, and these characteristics are dominant parameters for determining optimal operating conditions in engineering practice. The wastewater from simultaneous desulfurization and denitrification by MgO/ additive contains various ions such as Mg$^{2+}$, SO$_4^{2-}$, and NO$_3^-$, and the system is more complicated. Hence the previous researches can’t be used directly. The aim of this paper is to determine the optimum crystallization conditions of Mg$^{2+}$//SO$_4^{2-}$, NO$_3^-$·H$_2$O system by assessing the effects of various factors on crystallization yield, MSZW and crystal morphology; that is, the saturation temperature, the cooling termination temperature, the stirring rate and the cooling rate. The crystallization kinetics were also investigated. The economic and product quality parameters of wastewater recovery were combined to determine the optimal process conditions for the crystallization of Mg$^{2+}$//SO$_4^{2-}$ and NO$_3^-$·H$_2$O systems. The research results could improve the crystallization yield and the crystal form, and provide a theoretical basis for subsequent research into the Mg$^{2+}$//SO$_4^{2-}$, NO$_3^-$, Cl$^-$·H$_2$O system.

**EXPERIMENTAL**

**Materials and apparatus**

The reagents used in the experiments are analytical reagents (Aladdin Company, Shanghai). The mixed solutes in this paper consisted of anhydrous magnesium sulfate (MgSO$_4$) and magnesium nitrate (Mg(NO$_3$)$_2$) with a mass ratio of 6.2:1, which is consistent with the proportion of sulfate and nitrate ions in the simultaneous desulfurization and denitrification of wastewater. The experimental solution was prepared by weighing a selected amount of mixed solute with an electronic analytical balance (FA2004 model, precision ± 0.0001 g, Shanghai, China) followed by dissolving in deionized water.

The experimental setup is shown in Figure 1. The key apparatus is a closed double-layer glass crystallizer (S212-2, Jiangsu, China) with a volume of 2 L, in which the crystallization of the Mg$^{2+}$//SO$_4^{2-}$, NO$_3^-$·H$_2$O solution was carried out. A constant speed agitator (5GU3KB, 50–750 r/min) was used to mix the solution uniformly. The pH of the solution was determined by a pH meter (Raymond Model PHS-3E, Shanghai, China). The solution temperature was precisely controlled by an intelligent energy-saving thermostat.
(DC-2006, the temperature range is from -20 to 80 °C, ±0.1 °C, Scientz Biotechnology Company, Ningbo, China) with double temperature sensors. Firstly, the solution temperature was raised to a temperature of 5 °C above the saturation temperature and kept at that temperature for 60 minutes to ensure the solute dissolved completely. Then, the solution was cooled at a set cooling rate. The conductivity and temperature of the solution were monitored by a conductance meter (DDSJ-319 L, INESA Scientific Instrument Company, Shanghai, China). The computer monitored and recorded the initial nucleation conductivity values and temperatures. A circulating water multi-purpose vacuum pump (SHB-III, Henan, China) was used to separate crystal from the solid-liquid mixture after crystallization. The crystal was dried to a constant weight at 45 °C by an electric heating air drying oven (Type 101-3AB, ±1 °C, Beijing, China).

Analytical methods

The crystal composition was detected by X-ray diffraction (XRD, Bruker D8 Advance, Germany), with CuKα radiation (λ = 0.154056 nm), a scanning rate of 0.1°·s⁻¹, and incidence angles of 5–90° (2θ). The crystal morphology was determined by scanning electron microscopy (SEM, Hitachi S-4800, Japan). The static equilibrium method was used to measure the solubility of the mixed solute (Xiong et al. 2018).

The method used to calculate the crystallization yield is shown in Equation (1).

\[ \eta = \frac{C'}{C} \times 100\% \] (1)

where \( \eta \) – crystallization yield (%); \( C' \) – mass of the crystal after crystallization (g); \( C \) – mass of the initially mixed solute (g).

EXPERIMENTAL RESULTS AND ANALYSIS

Determination of solubility of the mixed solutes

The solubility of a mixed solute is a dominant parameter for determining MSZW during crystallization. However, the solubility of a mixture cannot be found in the literature due to it being affected by temperature, pressure, solutes composition and content. Therefore, obtaining the solubility of mixtures by a reliable method becomes an essential part of crystallization research.

Firstly, the reliability of the static equilibrium method for the determination of solubility was evaluated by using MgSO₄ as a test object under the existing experimental conditions (Figure S1(a)). The results show that the solubility measurement values are basically consistent with the literature values (Speight 2004), which proves the applicability of the static method and the reliability of the data. The solubility of the mixed solute determined by the static equilibrium method is shown in Figure S1(b).

It can be seen from Figure S1(b) that the total solubility of the mixed solutes increases with the increase of wastewater temperature, but they are less than the solubility of MgSO₄ under the same experimental conditions. It indicates that the solubility of MgSO₄ decreases significantly with the addition of Mg(NO₃)₂. Namely, Mg(NO₃)₂ has a salting-out effect on MgSO₄, which promotes the precipitation of MgSO₄·7H₂O crystals in the mixed wastewater.

Effect of saturation temperature on crystallization

Supersaturation is an important parameter in crystallization, which forms the driving force for nucleation and crystal growth. And it should be noted that saturation temperature


$(T_0)$ is a key factor for the formation of supersaturation. Therefore, the effects of various $T_0$ on crystallization in the saturated solutions were investigated (Figure 2). In the experiments, cooling termination temperature $(T_f)$ was 25°C, stirring rate $(S)$ was 300 rpm, cooling rate $(R)$ was 6°C/h, $T_0$ were from 30°C to 70°C with the increment of 10°C.

As can be seen from Figure 2(a) and 2(b), MSZW decreases and the crystallization yield increases with the increase of $T_0$ in the Mg$^{2+}$/SO$_4^{2-}$/NO$_3^-$-H$_2$O system. The reason is that with the increases of $T_0$, the ion concentration in the wastewater increases and the thermal motion intensifies. Thus, the collision probability between ions enhances, which promotes mass transfer and nucleation. It should be noted that the wastewater fails to nucleate spontaneously when $T_0$ is 30°C, because the initial mass fraction of the wastewater is low, and the supersaturation formed at the cooling termination temperature cannot promote nucleation. At the same time, when the MgSO$_4$·7H$_2$O crystals are formed, they will carry high crystal water, which makes the solution easy to reach supersaturation and difficult to form nuclei (Nemdili et al. 2018). Therefore, it is necessary to add seeds to reduce the energy barrier of nucleation and promote the formation of nuclei.

As shown in Figure 2(c) and 2(d), when $T_0$ is 70°C, the crystal is in the form of particles. When $T_0$ drops to 50°C, the supersaturation decreases, and the crystal grows in an acicular shape. This is mainly ascribed to that the nucleation rate and growth rate being positively correlated with the supersaturation. With the increase of supersaturation, the increment of the nucleation rate is faster than that of the growth rate (Tansel et al. 2018). Therefore, it is easy to obtain crystals with simple crystal form and small particle size under the high supersaturation.

It is obvious that $T_0$ has a significant effect on the crystallization yield and crystal quality. Consequently, it is especially important to select suitable $T_0$ during crystallization. In Figure 2(b), with $T_0$ rising from 30°C to 50°C, the crystallization yield is increased from 33.7% to 68.3%.

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![Figure 2](https://iwaponline.com/wst/article-pdf/doi/10.2166/wst.2019.341/613110/wst2019341.pdf)

**Figure 2** | Effect of saturation temperature on crystallization. (a) Effect of saturation temperature on MSZW. (b) Effect of saturation temperature on crystallization yield. (c) SEM image of a crystal with saturation temperature of 70°C. (d) SEM image of a crystal with saturation temperature of 50°C.
As $T_0$ further increases, the growth rate is slowed down, and the crystallization yield is increased slowly, whose increment is only 7.2%. Considering the energy consumption of the pretreatment-evaporation concentration of the wastewater crystallization, the optimal $T_0$ is selected as 50 °C.

**Effect of cooling termination temperature on crystallization**

The cooling termination temperature ($T_f$) may affect the yield and morphology of crystal products. Therefore, the effect of various $T_f$ on crystallization was investigated (Figure 3). In the experiments, $T_0$ was 50 °C, $S$ was 300 rpm, $R$ was 6 °C/h, $T_f$ was 10 °C, 15 °C, 20 °C, 25 °C, 30 °C.

Figure 3(a) shows MSZW increases from 11 °C to 12.9 °C as $T_f$ rises from 10 °C to 20 °C, then decreases to 11.4 °C as $T_f$ further increases to 30 °C. The fluctuations in MSZW all through the experiments, which are from 11 °C to 12.9 °C, are small, indicating that the change of $T_f$ has little effect on MSZW. Figure 3(b) shows that the crystallization yield increases linearly with the decrease of the cooling termination rate, with a maximum of 95.5%. It can be seen from the comparison of the two figures in Figure 3(c) and 3(d), the crystal still grows in an acicular shape, but the surface cracking is obvious after $T_f$ is dropped from 20 °C to 10 °C. The reason for this phenomenon is that the low termination temperature increases the supersaturation of the wastewater when the initial saturation concentration of the mixed wastewater maintains constant, thus the nucleation and growth rate of the crystal increases. Since the nucleation rate of the crystal is larger than the growth rate, the secondary nucleation rate of the crystal is increased. Finally, the supply of the solute is in short supply. At the same time, under the condition of a constant cooling rate, the decrease of the final termination temperature prolongs the crystallization time and increases the possibility of local stress concentration in the wastewater (Guo 2018). In consideration of the economics and crystal quality, $T_f$ should be chosen to be close to the normal...
temperature from the view of applications; therefore, 20 °C is selected as the optimal $T_f$.

**Effect of stirring rate on crystallization**

Stirring in the crystallization process can not only ensure the homogeneity of the wastewater and prevent crystal aggregates and agglomerate growth, but also play a decisive role in MSZW, crystallization yield and crystal morphology. The experimental results under various stirring rate ($S$) conditions are shown in Figure 4. In the experiments, $T_0$ was 50 °C, $T_f$ was 20 °C, $R$ was 6°C/h, $S$ was 200 rpm, 300 rpm, 400 rpm, 500 rpm, and 600 rpm.

Figure 4(a) and 4(b) shows that when $S$ is lower than 300 rpm, the increase of $S$ has little effect on MSZW; whereas, after $S$ is higher than 300 rpm, MSZW decreases significantly with the increase of $S$ and $S$ has little effect on the crystallization yield, which is maintained at about 78%. This is because the increase of $S$ accelerates the mass and heat transfer. Meanwhile, the impurities cannot be completely avoided during experiments. Stirring will promote the dispersion of the impurity particles in the solution system. Within moments of the solution changing to an unstable state during crystallization, the collision and agitation of the particles facilitate the formation of nucleation (Cheng et al. 2017). When $S$ is low, the driving force is small, the induction time of nucleation is long, and the variation of MSZW is low. Although the high stirring rate can reduce the nucleation barrier, the severe collision will lead to an increase in the secondary nucleation rate and the crystal breakage rate (Liu et al. 2019). Comparing Figure 4(c) with Figure 3(c), it can be discovered that the damage to the crystal becomes more obvious and the crystal size becomes smaller and more inhomogeneous as the stirring rate increases from 300 rpm to 600 rpm. Therefore, the selection of a suitable stirring rate is decisive for obtaining high-quality crystals. In this experiment, 300 rpm was selected as the optimal stirring rate.

![Figure 4](https://i2.wp.com/iwaponline.com/wst/article-pdf/doi/10.2166/wst.2019.341/113110/wst2019341.pdf)

*Figure 4* | Effect of the stirring rate on crystallization. (a) Effect of the stirring rate on MSZW. (b) Effect of the stirring rate on crystallization yield. (c) SEM image of a crystal with the stirring rate of 600 rpm.
Effect of cooling rate on crystallization

The selection of the cooling rate of the crystallization directly determines the speed of supersaturation formation, affecting the primary nucleation and productivity, therefore it is especially important for the crystallization process. The effects of various cooling rates \((R)\) on the crystallization were investigated (Figure 5). In the experiments, \(T_0\) was 50 °C, \(T_f\) was 20 °C, \(S\) was 300 rpm, \(R\) was 3 °C/h, 6 °C/h, 9 °C/h, 12 °C/h, 15 °C/h.

It can be seen from Figure 5(a) and 5(b) that as \(R\) accelerates, the crystallization yield is invariant at about 76%, but MSZW increases linearly. There are two reasons for this phenomenon. Firstly, the initial particle size of the formed nucleus is too small to be detected by the existing detection methods in real time. It needs an induction time to wait for the nucleus to grow to a detectable size. Thereby, the determination of the instantaneous temperature of the corresponding nucleus formation will also be delayed. The faster the \(R\) is, the more the temperature drops during the same induction time, the lower the instantaneous temperature measured is compared to that of the actual nucleation (Bian et al. 2019). As a result, the measured metastable zone is wider than the actual value. Secondly, the crystallization of the wastewater is significantly affected by the diffusion rate, which depends on the viscosity of the wastewater. With the increase in the cooling rate, the diffusion rate of solute to embryo becomes slower. Consequently, the nucleation rate becomes slower, which leads to the broadening of the metastable zone. Figure 3(c) with \(R\) of 6 °C/h illustrates that the crystal has less breakage but is not acicular; Figure 5(c) with \(R\) of 3 °C/h shows the crystal form is acicular. These experimental results indicate that the lower cooling rate is beneficial to the crystal morphology. However, if the cooling rate is too low, it will make the cooling time longer and consume more cooling energy, which is not beneficial for the economical operation. Therefore, the optimal cooling rate is selected as 6 °C/h.

Figure 5 | Effect of the cooling rate on crystallization. (a) Effect of the cooling rate on MSZW. (b) Effect of the cooling rate on crystallization yield. (c) SEM image of a crystal with the cooling rate of 3 °C/h.
Crystal composition analysis

$T_0$ and $T_f$ play a decisive role in the composition of crystal products. Therefore, XRD analysis of crystal products was carried out under the optimum operating conditions and the maximum operating conditions of $T_0$ and $T_f$, respectively. As shown in Figure 6, the crystal components are all MgSO₄·7H₂O, and no other substances are found. This is because the solubility of MgSO₄ is lower than that of Mg(NO₃)₂ at the same temperature, which makes MgSO₄ precipitate first in the cooling crystallization process.

As illustrated in Figure 5(b), the crystal yield can reach 78% with a solute mass of 28%. Zhang et al. (Zhang et al. 2011) conducted an experimental study on pure magnesium sulfate. According to their results, even at a solute mass of 34%, the crystal yield was only 53% at the same cooling termination temperature. Thus, it can be concluded that the presence of Mg(NO₃)₂ in the wastewater will not affect the crystal purity, but facilitate the salting-out of MgSO₄.

NUCLEATION DYNAMICS

The crystallization is controlled by both heat and mass transfer. The size, distribution and yield of crystal products depend on the speed and timing of nucleation. The nucleation order ($m$) and the solid-liquid interface energy ($\gamma$) not only reflect the difficulty of nucleation of solute in a supersaturated solution, $\gamma$ can also be used as an important thermodynamic parameter to investigate the process of crystal nucleation. Therefore, $m$ and $\gamma$ of various saturation temperatures were studied experimentally at the cooling termination temperature of 20 °C, stirring rate of 300 rpm and cooling rates of 3 °C/h, 6 °C/h, 9 °C/h, 12 °C/h and 15 °C/h, respectively.

Nucleation order

The Nyvlt (Nyvlt & Mullin 1970) equation is the earliest crystal nucleation equation, but the parameters in this equation have no physical meaning. In order to improve the Nyvlt equation, Sangwal (Sangwal 2009) proposed the Nyvlt self-consistent equation. The equation assumed that the nucleation rate $J$ is related to the maximum supersaturation of the power law equation near metastability and the equation is as in Equation (2).

$$J = K_f (\ln S_m)_m$$

where $J$ is the nucleation rate; $S_m$ is the nucleation supersaturation ratio; $m$ is the apparent nucleation order; and $K_f$ is the nucleation constant.

According to the theory of normal solution, the dependence of solubility on nucleation temperature can be described as in Equation (3).

$$\ln S_m = \ln \left( \frac{C_0}{C_m} \right) = \left( \frac{\Delta H_d}{R T_{m}} \right) \left( \frac{\Delta T_m}{T_m} \right)$$

where $\Delta H_d$ is dissolved enthalpy (J·mol⁻¹); $R$ is the ideal gas constant (J·mol⁻¹·K⁻¹); $T_m$ is the nucleation temperature (K). $C_m$ is the equilibrium concentration as the temperature is $T_m$; $C_0$ is the equilibrium concentration as the temperature is $T_0$; $\Delta T_m$ is the metastable zone width; $T_0$ is saturation temperature; $T_m$ is nucleation temperature.

The nucleation rate $f$ is proportional to the change rate of solution supersaturation, as shown in Equation (4).

$$f = \frac{\Delta C}{C_m \Delta T} = \frac{\Delta C}{C_m \Delta T} \frac{\Delta T}{\Delta T} = f \left( \frac{\Delta H_d}{R T_{0}} \right)$$

where $f$ is a constant representing the number of cores per unit volume; $R$ is the rate of cooling (K/h).

Equation (5) could be given by combining Equations (2)–(4).

$$\frac{\Delta T_m}{T_0} = \left( \frac{f}{K_f T_0} \right) \left( \frac{\Delta H_d}{R G T_m} \right)$$

Equation (6) can be obtained by taking the logarithm of Equation (5).

$$\ln \left( \frac{\Delta T_m}{T_0} \right) = \phi + \beta \ln R$$

where $\beta = \frac{1}{m}$, $\phi = \frac{1 - m}{m} \ln \left( \frac{\Delta H_d}{R G T_m} \right) + \frac{1}{m} \ln \left( \frac{f}{K_f T_0} \right)$.
According to Equation (6), \( \ln \left( \frac{\Delta T_m}{T_0} \right) \) is linear with \( \ln R \) when \( T_0 \) maintains invariant. When the slope \( \beta \) and the intercept \( \varphi \) are known, the nucleation order \( m \) and the parameter \( K_J \) related to the nucleation constant can be calculated.

The experimental results are shown in Figure 7 and Table 1.

The rank of the nucleation order \( m \) can directly reflect the formation mode of the crystal nucleus during crystallization. When \( m < 5 \), it is instantaneous nucleation, and when \( m > 3 \), it is progressive nucleation (Kashchiev et al. 2010). It can be seen from Table 1 that the apparent nucleation order of the \( \text{MgSO}_4-\text{Mg(NO}_3\text{)}_2 \) solution is almost independent of the saturation temperature \( (T_0) \), which is between 4.380 and 4.359, indicating that the nucleation mode is based on progressive nucleation. However, the parameter \( K_J/f \) related to the nucleation constant decreases with increasing \( T_0 \). Under the condition that \( m \) and the supersaturation ratio remain basically unchanged, the nucleation rate is proportional to the nucleation constant. The nucleation rate becomes faster, and the system metastable zone becomes narrower with the increasing of the nucleation constant. The above conclusion is consistent with the experimental results of the effect of initial cooling temperature on the metastable zone width of \( \text{MgSO}_4-\text{Mg(NO}_3\text{)}_2 \) solution.

### Solid-liquid interface energy

According to the classical nucleation theory (Sangwal 2010; Shiau 2018), the rapidly moving solute particles in the solution are first combined into a linear body and then grown to the embryo. After that, the solute particles are attached to the surface of the embryo. When the crystal embryo reaches a certain size, it establishes thermodynamic equilibrium with the solution and turns into the nucleus. As shown in Equation (7), the relationship between the established nucleation rate and the supersaturation ratio is described by the solid-liquid interface energy.

\[
J = A_f \exp\left( -B / \ln S_m \right)^2 = A_f \exp\left( -\frac{16\nu \pi^3}{3K_B T_m^2 \ln^2 S_m} \right)
\]  

where \( A_f \) is a constant related to the nucleation kinetics; \( K_B \) is the Boltzmann constant, \( 1.381 \times 10^{-23} \text{ J/K} \); \( \gamma \) is the solid-liquid interface energy \( \text{J/m}^2 \).

Combining Equations (3), (4) and (7) gives Equation (8).

\[
\left( \frac{T_0}{\Delta T_m} \right)^2 = F(1 - Z) \ln R
\]

where \( Z = -1 / \ln \left( \frac{f\Delta H_d}{A_f R_G T_0 T_m} \right) \);

\[
F = \frac{1}{Z} \left[ \frac{3}{16\pi} \left( \frac{K_BT_0}{2 RGT_0} \right)^3 \left( \frac{\Delta H_d}{RGT_0} \right)^2 \right]
\]

When \( T_0 \) is constant, \( \left( \frac{T_0}{\Delta T_m} \right)^2 - \ln R \) is linear, and the solid-liquid interface energy \( \gamma \) and \( A_f/f \) can be calculated by the slope -Z and the intercept F. The experimental results are shown in Figure 8 and Table 2.

It can be seen from Table 2 that with the increase of \( T_0 \), the parameter \( A_f/f \) related to nucleation is maintained almost unchanged. But \( \gamma \) is tending to decrease. The size of \( \gamma \) is directly related to the level of the nucleation energy barrier. The larger the value, the more difficult it is to nucleate, and the wider the metastable zone, which also illustrates the regularity of MSZW narrowing with increasing \( T_0 \).

<table>
<thead>
<tr>
<th>( T_0(\text{K}) )</th>
<th>( \beta )</th>
<th>( \varphi )</th>
<th>( m )</th>
<th>( K_J/f )</th>
</tr>
</thead>
<tbody>
<tr>
<td>313.15</td>
<td>0.229</td>
<td>-3.557</td>
<td>4.359</td>
<td>131.433</td>
</tr>
<tr>
<td>323.15</td>
<td>0.231</td>
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<td>4.328</td>
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<tr>
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<td>4.308</td>
<td>7581.733</td>
</tr>
<tr>
<td>343.15</td>
<td>0.2307</td>
<td>-4.353</td>
<td>4.335</td>
<td>37466.69</td>
</tr>
</tbody>
</table>
It is found out that with the increase of saturation temperature, the crystal morphology tends to be simple, the solid-liquid interface energy decreases, the nucleation rate increases, and the metastable region narrows; with the increase of the stirring rate and the decrease of the cooling rate, MSZW becomes narrower, and the crystal nucleus is more likely to form, but the high-speed stirring causes the crystal defects to be obvious. The cooling termination temperature has a significant effect on the crystallization yield, but the low temperature causes cracking of the crystal surface.

(3) The data of $\beta$, $\varphi$, $m$, $K_f$, $F$, $Z$, $\nu^{2/3}$ and $\gamma$ were obtained by experiments and the related theories. It can be concluded that as the $T_0$ increases, the nucleation order $m$ and the nucleation kinetic constant $A$ are basically unchanged, the nucleation constant $K_f$ increases, and the solid-liquid interface energy $\gamma$ decreases.

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