

# Crystal Nucleation of Single Tin Droplets Studied by Fast Scanning Calorimetry

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## **Abstract**

Crystal nucleation of single micro-sized tin droplets was investigated by in-situ experimental studies during rapid heating-cooling processes at rates up to  $4 \times 10^4$  K/s. For the first time the issue of separating the mutual effects of droplet size and cooling rate in rapid solidification has been solved. A theoretical model of these processes was developed on the basis of the classical heterogeneous nucleation theory and advanced then by a cavity induced heterogeneous nucleation model and cavity size dependent growth. It allows one to describe the cooling rate, droplet size and prior liquid overheating effects on crystal nucleation in single micro-sized tin droplets. This model is believed to be able to direct further research to shed more light on the nucleation mechanisms for metallic droplet solidification and related rapid solidification processes also beyond the particular system analyzed in this thesis.

## Zusammenfassung

Die Kristallkeimbildung eines einzelnen Zinntröpfchens von Mikrometergröße wurde durch in-situ Untersuchungen bei schnellen Heiz- und Abkühlprozessen mit Raten bis zu  $4 \times 10^4$  K/s untersucht. Dabei konnten erstmals die Auswirkungen von Tropfengröße und Abkühlraten bei rascher Kristallisation separiert werden. Ein theoretisches Modell der Kristallisation der Tropfen wurde auf der Grundlage der klassischen heterogenen Keimbildungstheorie entwickelt. Eine erste Variante dieses Modells wurde modifiziert, um heterogene Keimbildung induziert durch Hohlräume an den Grenzflächen zu berücksichtigen. Das von der Hohlraumgröße abhängige Wachstum konnte beschrieben werden. Dieses Modell hat es ermöglicht, die Abhängigkeit von Kristallkeimbildung in einzelnen Zinntröpfchen von Kühlrate, Tröpfchengröße und Überhitzung korrekt zu beschreiben. Wir erwarten, dass es im Rahmen der Weiterentwicklung dieses Modells möglich sein wird, die Mechanismen der Kristallkeimbildung für Metalltröpfchen und ihre schnelle Erstarrung sowie analoge schnelle Erstarrungsprozesse, auch über das spezielle in dieser Arbeit analysierte System hinaus, besser theoretisch beschreiben zu können.

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## ***Chapter 1 Summary***

## 1.1. Introduction

Nucleation in metallic materials plays a substantial role in most phase transformations. In industrial manufacturing processes nucleation determines many important aspects of the resulting microstructure and with that the final material properties [1-11]. During solidification undercooling is a key parameter related to crystal nucleation. Undercooling, also known as supercooling, is the process of lowering the temperature of a liquid below its melting point without solidification. It also describes the difference between theoretical and real phase transition temperatures. A high level of undercooling can result in structure refinement and then an increased spectrum of material properties can be obtained. In particular, much attention has been given to understand the processes involved in crystal nucleation and the resulting undercooling of metal droplets in solidification processes, e.g. gas atomization method [12, 13], drop tube method [14-17], electromagnetic levitation [18-20] and others [5, 21, 22]. The influence of nucleation on the solidification of droplets prepared by a droplet technique was commonly studied by Turnbull's classic method [23-27] which was originally developed by Vonnegut [28]. In these studies, the resulting undercooling was a key parameter to investigate the nucleation mechanisms of droplet solidification. One of the obvious facts arising from these studies is the rather large undercooling before the onset of nucleation during cooling of small and high-purity droplets. For micro-sized droplets it is commonly assumed that the occurrence of the first overcritical nucleus determines undercooling. In other words, once the first overcritical nucleus is formed, the nucleation of the whole droplet occurs immediately.

In 1950s, Turnbull developed the classical nucleation theory (CNT) for high-purity metal droplets, e.g. Ag, Ni, Cu, etc. [24-27]. His initial results suggested the attainment of homogeneous nucleation conditions in small metal droplets, but the obtained undercooling has subsequently exceeded this limit [10, 29, 30]. It indicates that the nucleation processes of small



metal droplets observed during solidification were still of heterogeneous nature. However, heterogeneous nucleation can be somehow avoided by rapid solidification methods leading to glass formation in many materials [31]. Yet, the current understanding of heterogeneous nucleation still remains insufficient, especially for rapid solidification processes, due in part to limitations of measurement capability. Hence, although the predictions of the classical nucleation theory have been supported in a few quantitative studies, there are still some important details that need to be resolved. In this thesis the effects of cooling rate (Paper 1), droplet size (Paper 2) and prior liquid overheating (Papers 3 and 4) on nucleation in rapid solidification will be discussed.

### 1.1.1. Cooling rate dependence on crystal nucleation

Based on the classical nucleation theory, the cooling rate dependence on undercooling, i.e. the appearance of the first overcritical nucleus depending on cooling rate, can be expressed by [32]:

$$\Delta T^{-2} = \frac{16\pi\sigma_{ls}^3 v^2 T_l^2}{3kT_n \Delta H_V^2 \ln[10^{-3} d^3 (\sigma_{ls}/a_0)^2 (a_0/v) D_l \Delta T^{-1}/q_c]} \quad (1.1)$$

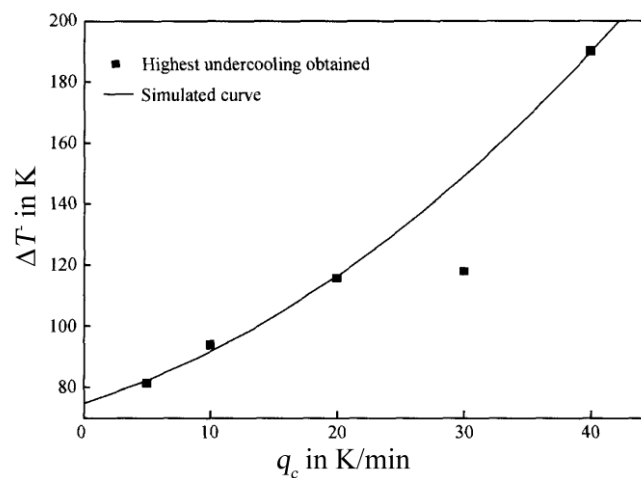
where  $\Delta T$  is the undercooling,  $\sigma_{ls}$  is the solid-liquid interfacial energy,  $v$  is the atom volume,  $T_l$  is the liquidus temperature,  $k$  is Boltzmann constant,  $\Delta H_V$  is the latent heat per unit volume,  $T_n$  is the nucleation temperature,  $d$  is the droplet diameter,  $a_0$  is the atomic spacing,  $D_l$  is the liquid diffusivity and  $q_c$  is the cooling rate. Due to many unknown parameters in this equation, it is difficult to investigate the cooling rate dependence on undercooling quantitatively. On the other hand, it is impossible to distinguish the mutual effects of cooling rate and droplet size on undercooling according to this equation.

Another attempt to investigate the relationship between undercooling and cooling rate was realized by Acrivos and yields [33]:

$$\Delta T^{-2} = Aq_c, \quad (1.2)$$

where  $A$  is a constant depending on the system being solidified. The equation should be valid for any composition invariant transformation in which the nucleation process can be described by the classical nucleation theory [33]. But this equation is incorrect for two critical cases. First, undercooling increases with increasing cooling rate infinitely. Second, the degree of undercooling equals to zero under the condition of the equilibrium solidification, i.e. the cooling rate is zero, which doesn't obey the nature of nucleation.

Later, Li *et al.* [34] studied the undercooling of germanium melts by differential scanning calorimeter (DSC) combined with flux (dehydrated  $B_2O_3$ ) processing and obtained the relationship between undercooling and cooling rate. They found that the undercooling increased with increasing cooling rate in the range from 5 to 40 K/min, as shown in Fig. 1.1. Yu *et al.* [35-37] also obtained similar results for Ni based alloys. However, knowledge gained about the influence of cooling rate from these studies was limited due to the small accessible cooling rate range.



**Fig. 1.1** Relation between the undercooling and cooling rate of a Ge melt [34].

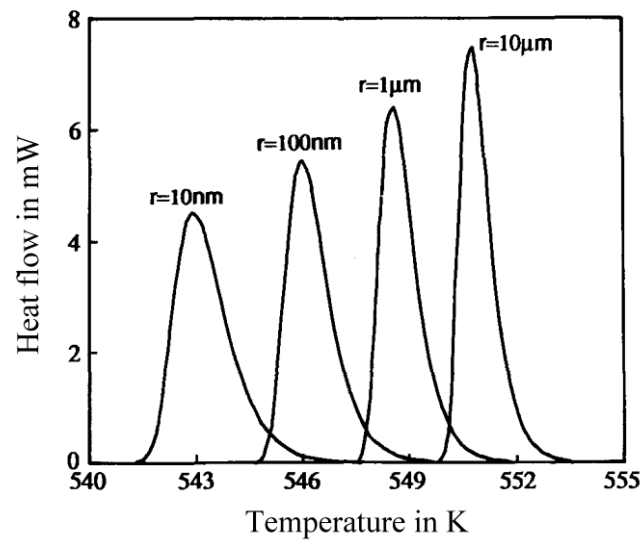
Consequently, certain limitations exist for the investigation of cooling rate effect on crystal nucleation: (i) lack of a sufficient theoretical model for micro-sized metal droplets during rapid solidification, (ii) it is hard to separate the mutual effects of cooling rate and droplet size on undercooling and (iii) commonly the measurements are performed in a too narrow cooling rate range.

### 1.1.2. Droplet size dependence on crystal nucleation

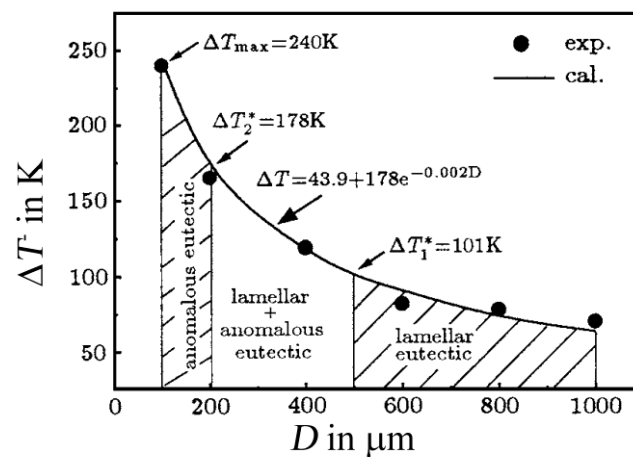
The accessible undercooling can be increased by decreasing droplet size [38-41], i.e. the temperature of the appearance of the first overcritical nucleus decreases with decreasing droplet size. Some experimental studies have been carried out on the droplet size effect on undercooling of micro-sized droplets. For example, Sheng *et al.* [38] evaluated the relation between undercooling and droplet size in Al-based mixtures. They have found that smaller droplet size can cause deeper undercooling. However, commonly a droplet ensemble was necessary for this kind of measurements and as a result the droplet size distribution had to be taken into account [42-44]. In order to overcome this drawback, Perepezko *et al.* [5, 21] has studied the nucleation kinetics of Al and Au single droplets, but they did not focus on the size effect on undercooling of crystal nucleation.

Some other studies have been carried out to theoretically calculate the droplet size effect on undercooling [40, 45, 46]. Cantor *et al.* [45] simulated the solidification exothermal peaks of different droplets in size with radius of 10 nm, 100 nm, 1  $\mu\text{m}$  and 10  $\mu\text{m}$  in DSC measurements, as shown in Fig. 1.2. They found that the droplet size effect on undercooling exists from microscale to nanoscale. Wei *et al.* [46] calculated the solidification undercooling of Al-Ge alloy droplets by establishing a theoretical model and obtained the relationship

between the undercooling and droplet size, as shown in Fig. 1.3. It can be seen that the undercooling increases nonlinearly with decreasing droplet size.



**Fig. 1.2** Calculated droplet solidification exothermal peaks for four different droplets size in the range from 10 nm to 10  $\mu\text{m}$  with a contact angle of  $40^\circ$  and  $10^{19} \text{ m}^{-2}$  potential catalytic nucleation sites at the cooling rate of 10 K/min [45].



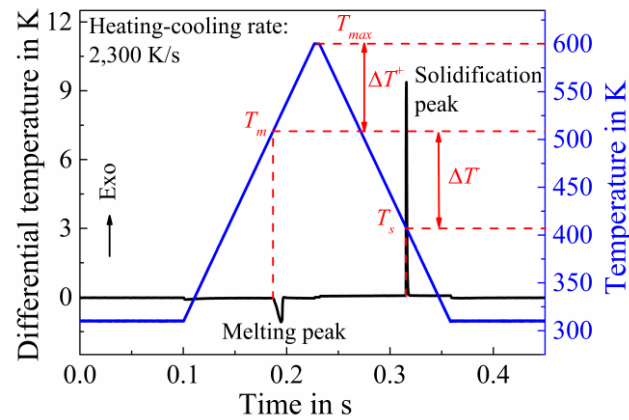
**Fig. 1.3** Droplet undercooling and eutectic morphology versus droplet diameter [46].

For rapid solidification, only few studies were carried out. Zhai *et al.* [47] investigated the droplet size dependence on undercooling of rapid-quenched Sn-Bi eutectic alloy droplets by an indirect method, i.e. microstructure analysis. The results showed that the undercooling significantly increased with decreasing droplet size under the condition of rapid solidification.

Consequently, such studies of droplet size effect on crystal nucleation still have certain limitations: (i) need to consider the droplet size distribution, (ii) commonly the measurements are performed at low cooling rates and in a too narrow cooling rate range and (iii) indirect characterization of the nucleation process after complete solidification, i.e. by microstructure analysis.

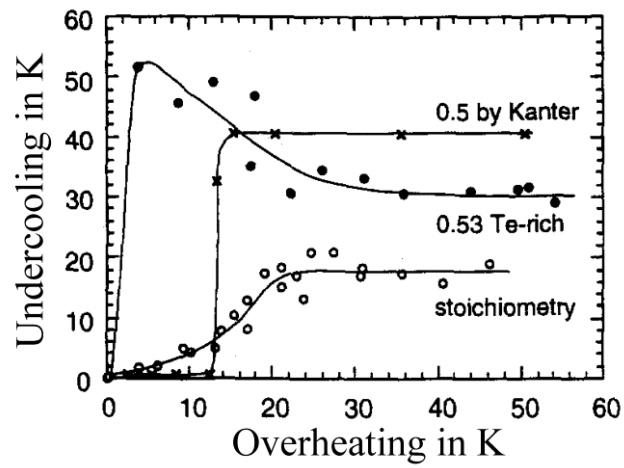
### 1.1.3. Overheating dependence on crystal nucleation

In metal droplets the degree of overheating ( $\Delta T^+$ ) of a melt prior to its subsequent undercooling ( $\Delta T^-$ ) and resulting crystallization has been demonstrated to play a significant role in determining the nucleation process [48-52]. Here  $\Delta T^+ = T_{max} - T_m$  is the difference between the maximum temperature,  $T_{max}$ , reached in prior overheating of the liquid and the melting temperature,  $T_m$ ,  $\Delta T^- = T_m - T_s$  is the difference between melting temperature and the particular temperature  $T_s$  where solidification is observed experimentally. The meaning of both these parameters is illustrated in more detail in Fig. 1.4 for one particular heating and cooling process.

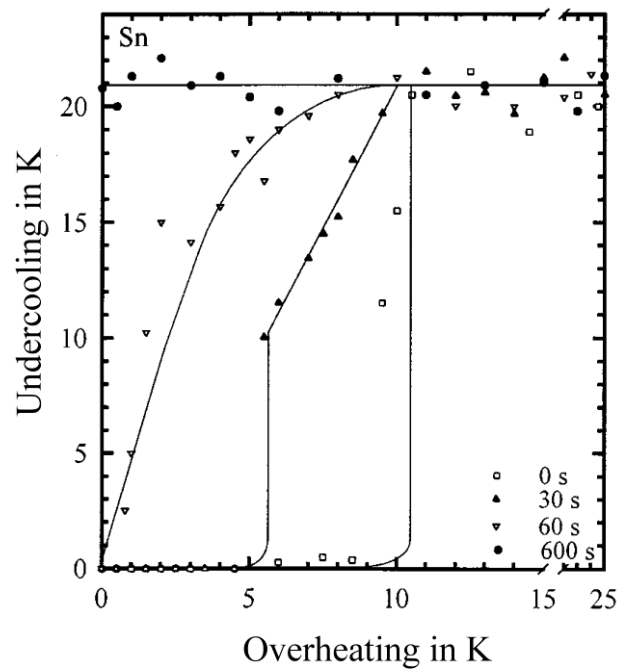


**Fig. 1.4** Typical temperature profile (blue line) to study the influence of liquid overheating on undercooling and a measurement curve (black line) by differential fast scanning calorimetry [53].

There have been numerous reports concerning the influence of melt overheating on the subsequent undercooling behavior during cooling both in terms of the level of overheating and the duration (holding time) [48-51, 54, 55]. Rudolph *et al.* [50] investigated the overheating-undercooling relationship by experiments in Bridgman ampoules. The results showed a distinct increase in the degree of undercooling in stoichiometric CdTe melts being overheated in excess of a critical value above the melting points, as shown in Fig. 1.5. Tong *et al.* [55] studied the dependence of undercooling of Sn melts preceding the onset of solidification on the level of liquid overheating above its melting temperature measured by DSC, as shown in Fig. 1.6. It is demonstrated that the dependence of  $\Delta T^-$  on  $\Delta T^+$  can be either abrupt or continuous, depending on the length of holding time. In a special case a linear relationship between the undercooling and prior liquid overheating was found.

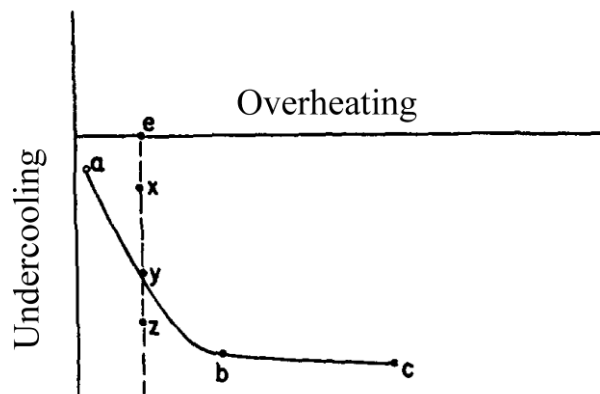


**Fig. 1.5** Dependence of undercooling on overheating in stoichiometric and non-stoichiometric CdTe with 1 and 5 at% Te excess after a constant holding time of 1 h in the molten state [50].



**Fig. 1.6** Variations of undercooling as a function of overheating for different holding time for Sn. Corresponding holding time: 0, 30, 60 and 600 s [55].

While these effects have been interpreted in relation to the change in the liquid structure, there is no direct evidence supporting this proposal. Instead, an original model developed by Turnbull [56] has provided a useful framework to interpret the influence of overheating temperature on the observed undercooling behavior. Based on the assumption of the existence of cavities, Turnbull [56] developed a theory of the cavity induced heterogeneous nucleation mechanism. As shown in Fig. 1.7, this approach predicts a linear relationship,  $\Delta T^-/\Delta T^+ = \tan\theta$ , between accessible solidification undercooling and prior liquid overheating, where  $\theta$  is the contact angle between the liquid and solid phases. In the region of the curve  $ab$  which usually extends only a few degrees above the melting temperature,  $\Delta T^-$  is strongly dependent upon  $\Delta T^+$ , while in the region of the curve  $bc$ ,  $\Delta T^-$  reaches a constant which is independent of  $\Delta T^+$ . Turnbull's predictions have been analyzed in a variety of experimental analysis. Most of these studies, however, only address nucleation at low cooling rates measured by thermal analysis devices [49, 54, 55] or without cooling rate control [52, 56].



**Fig. 1.7** Effect of overheating on undercooling in liquid-solid phase transition [56].

Consequently, such studies of liquid overheating effect on crystal nucleation still have certain limitations: (i) no direct evidence supports that the effect is in relation to the change in



the liquid structure, (ii) commonly the measurements are performed at low cooling rates or without cooling rate control.

## **1.2. Objectives and structure of the thesis**

In summary, the nucleation of metal droplets, which requires undercooling of the liquid below its melting point, has been extensively investigated under near-equilibrium, isothermal and steady-state conditions as mentioned above. Traditional industrial manufacturing processes, such as casting, have been modeled based on near-equilibrium thermodynamic concepts. It is assumed that the liquid, the solid and the solid-liquid interface exist above, below and at the melting point, respectively. However, the understanding of nucleation or solidification under the far from equilibrium or extremely non-isothermal conditions that are currently accessible due to the development in rapid quenching technology, such as 3D printing, pulsed lasers and splat quenching, is still evolving. As a result, the uncertainties in most studies of small micro-sized droplets continue to be the major barrier to a more complete understanding and the development of the design strategies of technical processes, e.g. gas atomization, 3D printing or laser forming, instead of time-consuming empirical approaches applied in most industrial settings.

Furthermore, there are still some open questions regarding the three crucial factors determining the degree of accessible undercooling of crystal nucleation, i.e. cooling rate, droplet size and overheating dependences on crystal nucleation, in the solidification of small droplets, especially during rapid solidification. (i) Due to the inherent non-transparency of metals, combined with high temperature conditions during their heating or cooling processes, the characterization of the nucleation process is usually performed only after complete

solidification by microstructure analysis. (ii) Most experiments only address nucleation at low cooling rates measured by conventional thermal analysis devices. For faster cooling processes in micro-sized metal droplets theoretical models are the only possibility to gain information about nucleation kinetics. (iii) Most of the measurements were performed on ensembles of droplets with by necessity different sizes and not on single droplets. Therefore, in such studies the droplet size distribution had to be taken into account in the evaluation of the results. The necessity to take the droplet size distribution into account is a severe limitation for this kind of measurements attempting to evaluate the size effect on the nucleation process of droplets. (iv) Otherwise, it seems to be hard to evaluate the effects of cooling rate and droplet size on undercooling separately. (v) The overheating dependence on undercooling has been interpreted in relation to changes in the liquid structure, but there is no direct evidence supporting this proposal. Hence, the relationship between undercooling of crystal nucleation and overheating has not been specified or explained in a sufficiently comprehensive form.

In order to solve these open questions, the nucleation processes of single micro-sized metal droplets at high cooling rates need to be characterized. Based on Turnbull's classical approach for the investigation of the nucleation processes of droplets, the undercooling required for nucleation, i.e. the specific temperatures of liquid-solid phase transition including melting and nucleation temperatures, need to be in-situ measured. So new devices with high sensitivity and high scanning rates are required.

With the development of nanotechnology and micro-electro mechanical systems (MEMS), it is possible to fabricate calorimeter sensors that are able to measure samples with nanogram masses and energies less than one nanojoule [57-59] or even picojoule [60]. These developments enable the possibility of considerably enlarging and controlling the scanning rates. Therefore, thermal analysis method, i.e. nanocalorimetry (e.g. differential fast scanning

calorimetry (DFSC) [61, 62] in the research of this thesis), can provide a useful tool in the determination of nucleation kinetics for the solidification of micro-sized metal droplets at controllable high cooling rates up to  $10^4$  K/s [63-65]. So one single micro-sized droplet measurement can be performed and then allow for the distinction the effects on the crystal nucleation between cooling rate and droplet size from different nucleation mechanisms. In particular, it can also reveal the nature of the nucleation process for one droplet size with various overheating. Therefore, the developments of advanced calorimetric devices allow the testing of available theories for small micro-sized droplets under far from equilibrium conditions. Moreover, it may improve the corresponding development of new theories or consistent implementation of existing theories.

With this in mind the following areas for experimental and theoretical investigation are focused on in the papers of Chapter 2:

- 1) Cooling rate dependence of crystal nucleation in single micro-sized droplets (see Paper 1);
- 2) Droplet size dependence of crystal nucleation (see Paper 2);
- 3) Prior liquid overheating dependence of crystal nucleation (see Papers 3 and 4).

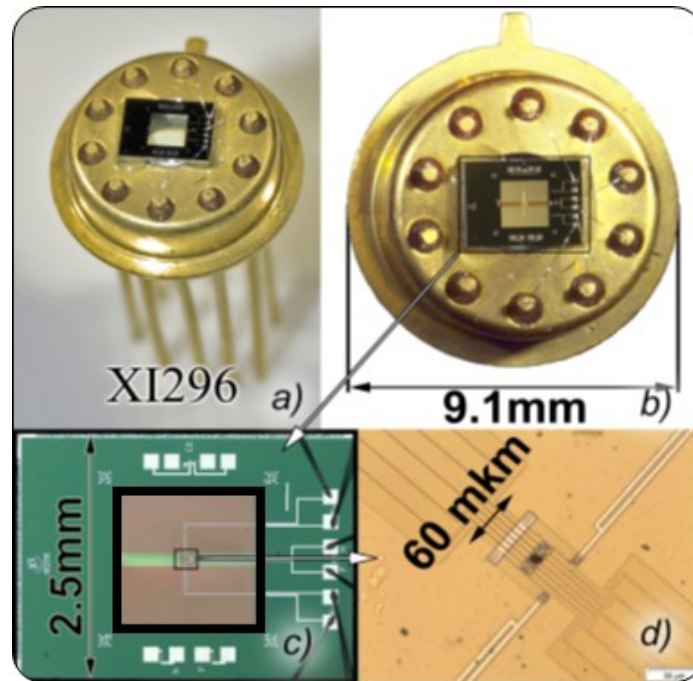
### **1.3. Differential fast scanning calorimetry**

In 2009, the undercooling of one single micro-sized droplets was successfully measured in-situ by a differential fast scanning calorimeter firstly by us (for details see Appendix A1) [63], and its repeated nucleation mechanism at a high cooling rate ( $10^4$  K/s) was discussed by a statistic method (for details see Appendix A2) [65]. In these studies challenges of such experiments like calibration, heat transfer limitations, sample placement on the sensor and the

repeatability of high rate experiments were focused on. These studies were the basis for the successful approach to solve the open questions listed above. Later, this technique was employed for studies of nucleation processes [64] and microstructure [66-68] of single micro-sized metal droplets in a wide range of cooling rates. So the differential fast scanning calorimetry (DFSC) provides ultrahigh but controllable cooling rates without changing the shape of droplets [65], making it possible to study the dependences of cooling rate (Paper 1), droplet size (Paper 2) and liquid overheating (Papers 3 and 4) on crystal nucleation by in-situ measurements. In this section a short introduction of DFSC is provided.

DFSC based on thin film sensors with extremely small measuring area extends scanning rate range at cooling significantly. For the sensors used in this thesis heat losses through the gas are about ten times larger than the losses through the 0.5  $\mu\text{m}$  thick freestanding  $\text{SiN}_x$  membrane [69]. DFSC uses high sensitive, low addenda heat capacity thin film sensors. For example, the sensor XI-296 (Xensor, The Netherlands) [58, 63, 70, 71] consists of a Si frame  $2.5 \times 5 \text{ mm}^2$  fixed on a standard integrated circuit housing, as shown in Fig. 1.8. The actual calorimeter consists of two heaters and six semiconducting thermopiles embedded in the measurement (heated) area, whose size is about  $60 \times 80 \mu\text{m}^2$ . For DFSC experiments the single droplet must be placed in the center of the measurement area and must be also in direct contact with the thermopiles to obtain the necessary signal to noise ratio. Then reliable information about sample temperature for a small droplet can be obtained. Otherwise the strong temperature gradient outside the heated area influences the measurement [72] and uncertainty of temperature measurement increases dramatically. The temperature profile inside the measurement area is basically homogeneous in which the temperature difference is in the range of a few Kelvin [61, 72-74]. For the measurements in this thesis the thermopiles of the calorimeter was calibrated with flat indium, lead and tin samples of about several micron thickness. For ideally placed samples accuracy of the temperature measurement is about  $\pm 5 \text{ K}$  and repeatability about  $\pm 1 \text{ K}$ .

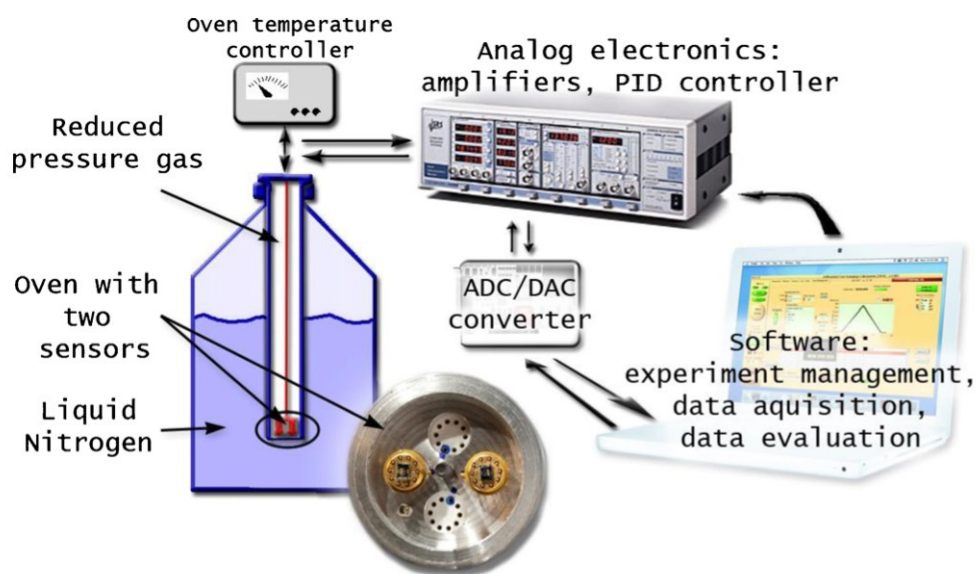
[63]. Consequently, DFSC opens up a new in-situ method to reveal the crystal nucleation and other phase transitions in metallic samples at cooling rates up to  $10^4$  K/s, making it possible to compare the theoretical estimation for rapid solidification with experimental results.



**Fig. 1.8** Measuring cell of the calorimeter. Xensor Integration gauge XI296 [63, 71]. (A) and (B) show the whole sensor, (C) - the silicon frame and (D) - the heated area on the freestanding membrane in the center of the chip sensor.

Fig. 1.9 shows a power compensated differential fast scanning calorimeter with a wide range of heating-cooling rate upon  $10^6$  K/s or more. Thin film sensors are placed in an oven at the bottom of a tube in a gas environment, such as air,  $N_2$ , He, Ar and so on, rather than in vacuum. Heaters and thermopiles are connected to analog electronic devices. The electronics is driven from a computer by a fast ADC/DAC board, which is used for the temperature setpoint determination and data collection. The electronic devices are controlled by self-developed

software which is also used for data collection/evaluation, for details see Ref. [61]. Until now this is the only technique that is capable of applying both controlled heating and controlled cooling at rates up to  $10^6$  K/s [58]. For metallic materials, it allows both heating and cooling with rates from 5 to  $10^5$  K/s. This interval was of particular interest for the nucleation of metallic materials because it covers the technologically relevant range of heating and cooling rates for common and rapid nucleation processes of metallic materials.



**Fig. 1.9** Schematic illustration of the differential fast scanning calorimeter setup [61].

#### **1.4. Theoretical estimation of the crystal nucleation of single micro-sized droplets**

In Chapter 2, the nucleation processes of single micro-sized tin droplets were in-situ measured at high cooling rates. For the first time the effects of droplet size and cooling rate on droplet nucleation were successfully separated by experiments and theoretical analysis (see

Papers 1 and 2). Then the more complex case of the relationship between prior overheating and undercooling was studied in rapid solidification processes (see Papers 3 and 4). In a first attempt a theoretical model was developed on the basis of the classical heterogeneous nucleation theory and supplemented by the cavity induced heterogeneous nucleation model and cavity size dependent growth. Hence, in this section the theoretical estimation of the crystal nucleation of single micro-sized droplets will be introduced.

Crystal nucleation is a process that involves the formation of clusters of atoms as embryos. These embryos are different in size and each may be considered as a possible nucleus for the formation (growth) of the new phase. Generally, based on the classical nucleation theory developed by Turnbull [25, 27, 56, 75], there are two kinds of nucleation mechanisms in terms of the different nucleation ways: homogeneous and heterogeneous nucleation. Homogeneous nucleation involves the formation of a nucleus without the influence of any catalytic heterogeneous sites such as the extraneous impurities, internal solid phases in the melt and so on, while heterogeneous nucleation requires an association with these catalytic sites. In the case of the single micro-sized tin droplets measured by DFSC in this thesis, the nucleation way of the single droplets is the surface and bulk heterogeneous nucleation.

For continuous cooling, the nucleation rate becomes time  $t$  or temperature  $T$  dependent. By this reason, the total number of nuclei formed in the given volume  $V$  or surface area  $S$  of the tin droplet during cooling from onset melting temperature  $T_m$  to onset nucleation temperature  $T_n$  at a constant rate  $q_c$  is given by

$$N = \int (J_V V + J_S S) dt = \frac{1}{q_c} \int_0^{\Delta T^-} (J_V V + J_S S) d\Delta T^-, \quad (1.3)$$

where  $\Delta T^- = T_m - T_n$  is the actual undercooling which may vary from zero, and  $J_V$  and  $J_S$  are the nucleation rates in the bulk and on the surface, respectively. In addition, it is assumed that the

growth process proceeds at a high rate which implies that the nucleation of the droplet occurs immediately after the first overcritical nucleus is formed, i.e. the accessible undercooling (or the temperature  $T_n$ ) can be determined from the condition  $N = 1$ .

Based on the classical nucleation theory, a modified expression (see Papers 1 and 2) for the nucleation rate of the single droplet during a rapid cooling process was given in the form

$$J_s = \frac{n_s \Phi (1 - \cos \theta_{0s})}{\Delta T^{-2}} \exp \left( - \frac{\Psi f(\theta_{0s})}{(T_m - \Delta T^-) \Delta T^{-2}} \right), \quad (1.4)$$

for the surface nucleation and

$$J_v = \frac{n_v \Phi (1 - \cos \theta_{0v})}{\Delta T^{-2}} \exp \left( - \frac{\Psi f(\theta_{0v})}{(T_m - \Delta T^-) \Delta T^{-2}} \right) \quad (1.5)$$

for the bulk nucleation with

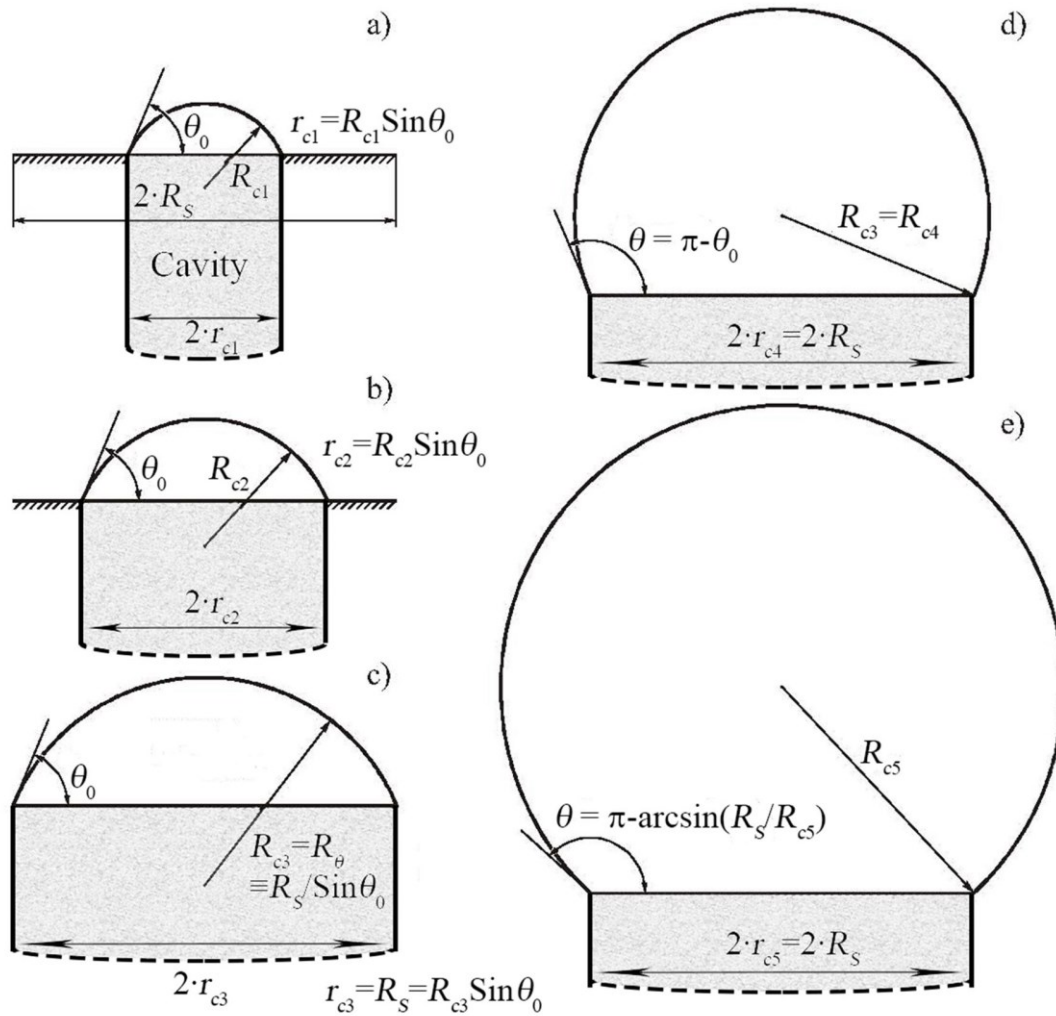
$$\Phi = \frac{D_l}{a_0^2} \frac{8\pi\sigma_{ls}^2 T_m^2}{a_0^2 \Delta H_v^2}, \quad (1.6)$$

$$\Psi = \frac{16\pi\sigma_{ls}^3 T_m^2}{3k\Delta H_v^2}, \quad (1.7)$$

$$f(\theta_{0s,0v}) = \frac{1}{4} (2 - 3 \cos \theta_{0s,0v} + \cos^3 \theta_{0s,0v}), \quad (1.8)$$

where  $n_s = C_{is}/a_0^2$  and  $n_v = C_{iv}/a_0^3$  are the numbers of heterogeneous nucleation sites of the catalytic surface area per unit surface and per unit volume, respectively. Those numbers can be also denoted as the density of nucleation sites ( $C_{is}$  and  $C_{iv}$  are the surface and bulk impurity concentrations, respectively).  $f(\theta_{0s,0v})$  is the catalytic activity which describes the catalytic potency of the heterogeneous nuclei and  $\theta_{0s,0v}$  is the contact angle on the surface of the heterogeneous nucleation site, as shown in Fig. 1.10.





**Fig. 1.10** Schematic illustration of the change of the contact angle on the heterogeneous nucleation site [53].

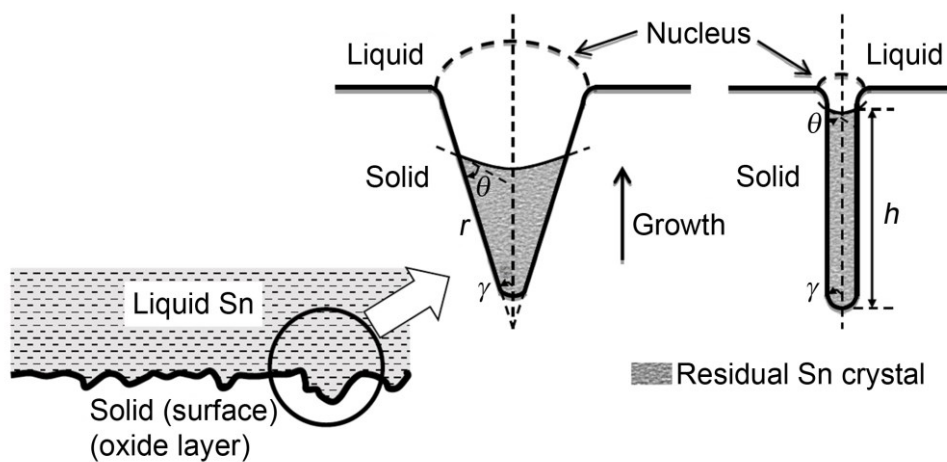
For a small radius of the nucleus, the contact angle,  $\theta_0$  is constant when the critical radius of the crystal nucleus is less than the radius of the heterogeneous nucleation site with fixed size,  $2R_s$  (Fig. 1.10(a)). The contact angle does not change with increasing radius of the nucleus (Fig. 1.10(b)), until the border of the nucleus reaches the edge of the nucleation site. There are two contact angles in this case for the same radius of nucleus:  $\theta_0$  and  $\pi - \theta_0$  (Fig. 1.10(c) and 1.10(d)). Undoubtedly, this case is realized only if  $\theta_0 < \pi/2$ . When the critical radius of the nucleus  $R_c$  is

larger than the crossover radius  $R_\theta = R_S/\sin\theta_0$ , the contact angle increases sharply (Fig. 1.10(e)).

In such case, the catalytic activity of such nucleation site diminishes.

According to this modified model of the classical nucleation theory, the cooling rate and droplet size dependences on crystal nucleation of single micro-sized droplets in rapid cooling can be interpreted. However, the nucleation dependence of liquid overheating is more complex, which has so far not been defined or explained completely even Turnbull [56] developed the theoretical description already more than 60 years ago. So in Papers 3 and 4 a theoretical model was developed on the basis of the cavity induced heterogeneous nucleation model and cavity size dependent growth.

Based on the assumption of the existence of cavities, a cylindrical or conical cavity on the droplet surface in its oxidation layer is considered, as suggested in the principal features of the cavity induced heterogeneous nucleation mechanism first suggested by Turnbull [56], as shown in Fig. 1.11. In this approach, the overheating effect on the value of the accessible undercooling can be explained by considering in detail the evolution of a cavity generated nucleus in differently sized cavities during cooling.



**Fig. 1.11** Schematic illustration of remaining crystals in conical and cylindrical cavities [53].

In the development of this model, the following assumptions are made about the nucleation mechanism which is expected to dominate the heating-cooling process. (i) The nucleation of the single Sn droplet is caused by both bulk and surface heterogeneous nucleation. (ii) During cooling the remaining solid Sn crystal in the cavity regrows to the top of the cavity and then acts as a nucleus. It means that the nucleation process is controlled by the regrowth of the remaining solid Sn crystal when the cooling rate is higher than a critical value. (iii) When the cooling rate reaches the critical value, the remaining solid is fully melt and regrows from the bottom to the top of the cavity during cooling. (iv) When the cooling rate is less than a critical value, there is a competition of time between the regrowth of the remaining solid Sn crystal in the cavities and nucleation in the droplet surface or bulk. (v) The amount of the remaining solid Sn crystal is also related with the level of liquid overheating. When the overheating is high enough, the solid Sn crystal in the cavities is fully melt, and vice versa.

Combined with the modification model of the classical nucleation theory, the size of the mouth of the cavities  $r_c$  can be calculated, as shown in Fig. 1.10(a) - (e). When the radius of the cavity  $r_c$  is smaller than  $R_s$ ,  $r_c$  can be calculated by  $r_c = R_c \cdot \sin \theta_0$  (Fig. 1.10(a) and (b)). Until the border of the cavity reaches the edge of the nucleation site,  $r_c$  is equal to  $R_s = R_\theta \sin \theta_0$  (Fig. 1.10(c) - (e)).

## 1.5. General conclusions

In this thesis the aspects of crystal nucleation in the rapid solidification of single micro-sized Sn droplets via differential fast scanning calorimetry were investigated. The results have shown that the dependences of cooling rate, droplet size and liquid overheating on crystal nucleation are quantitatively described by a modified classical nucleation theory. Specifically,

bulk and surface heterogeneous nucleation with the cavity induced heterogeneous mechanism and the size-dependent regrowth of the residual crystal in cavities are taken into account during the rapid solidification process of single Sn droplets. In the next sections the cooling rate (Paper 1), droplet size (Paper 2) and liquid overheating (Papers 3 and 4) effects on crystal nucleation are concluded.

### **1.5.1. Cooling rate effect on crystal nucleation**

In Paper 1 in-situ experimental studies during rapid heating and cooling processes at rates from 20 to  $4 \times 10^4$  K/s were performed by non-adiabatic power compensated differential fast scanning calorimetry, which covering the cooling range of common and rapid solidification. An adequate description within the modified model of the catalytic property of heterogeneous nucleation sites was envisaged. The experiments, providing the needed input data for the theoretical description, can be achieved by DFSC developed in our group.

In Paper 1 a tin droplet with diameter about 10  $\mu\text{m}$  was chosen to study the nucleation kinetics at cooling rates in the range from 20 to  $4 \times 10^4$  K/s. The nucleation behavior of one single tin droplet at rapid cooling rates is revealed. It is found a shelf-like dependence on undercooling of crystal nucleation. In other words, there is an obvious change of undercooling between 300 and 1000 K/s implying that two different nucleation mechanisms, i.e. bulk and surface heterogeneous nucleation, do exist in the solidification of this droplet. Bulk heterogeneous nucleation occurs on the impurities in the internal of the droplet and surface heterogeneous nucleation is stimulated by the catalysts distributed in the droplet surface. This behavior is much different compared with that measured by DSC [41].

In Paper 1 it is also shown that the heterogeneous nucleation mechanism changes from surface nucleation to bulk nucleation with increasing cooling rate. For this study, the transition

interval is between 300 and 1000 K/s in which surface and bulk nucleation act simultaneously. If the cooling rate is less than 300 K/s, the surface nucleation is predominant while bulk nucleation is dominated at cooling rates higher than 1000 K/s. Apart from the change of nucleation mechanisms, both the surface and bulk nucleation are related to the droplet size.

### **1.5.2. Droplet size effect crystal nucleation**

Next, the inner mechanisms of the size and cooling rate dependences on nucleation in single tin droplets were elucidated separately in Paper 2. Based on the classical nucleation theory, the physical origin of heterogeneous nucleation catalysis was explored and the two different heterogeneous nucleation mechanisms, surface and bulk, were put forward. It was deemed that the nucleation behavior was related to the size of the catalytic site. When  $R_c$  is smaller than the size of the catalytic site the contact angle is constant. If  $R_c$  is larger than the size of the catalytic site, the contact angle increase sharply and the catalytic activity decreases. According to this assumption, the theoretic equations of the nucleation rates of surface and bulk heterogeneous nucleation are modified. With this modification, the cooling rate dependence on undercooling for single droplets with different sizes were successfully described. In this paper the diameter of the investigated tin droplets varied in the range from 7 to 40  $\mu\text{m}$  at the cooling rates from 100 to 14,000 K/s. For droplets smaller than 40  $\mu\text{m}$ , both the surface and bulk nucleation are active during the solidification process. Moreover, the cooling rate range of the transition from surface nucleation to bulk nucleation shifts to higher cooling rate with increasing droplet size. However, the 40  $\mu\text{m}$  diameter droplets shows a different nucleation behavior. Surface nucleation acts at low cooling rates, and then surface and bulk nucleation act almost simultaneously with increasing cooling rate.

### 1.5.3. Influence of prior liquid overheating on crystal nucleation

In Papers 3 and 4 the relationship between prior liquid overheating and subsequent undercooling was studied by DFSC at cooling rates from 500 to  $10^4$  K/s. It is observed experimentally that (i) the degree of undercooling increases first gradually with increase of prior liquid overheating; (ii) if the degree of prior liquid overheating exceeds a certain limiting value, then the accessible undercooling increases always with increasing cooling rate; (iii) in the alternative case of moderate initial overheating, the degree of undercooling reaches an undercooling plateau; and (iv) in latter case, the accessible undercooling increases initially with increasing cooling rate. However, at a certain limiting value of the cooling rate this kind of response is qualitatively changed and the accessible undercooling decreases strongly with a further increase of cooling rate.

In Papers 3 and 4 the theoretical interpretation for these unexpected behavior is performed. Based on the theory of cavity induced heterogeneous nucleation developed by Turnbull [56], size-dependent growth of the residual solid tin in the nano-sized cavities was incorporated. It is deemed that an oxide layer covers the droplet surface because the measurements were performed in air and the heat of formation for  $\text{SnO}_2$  is large, which produces a large amount of cavities at the droplet surface. Because of the hydrostatic pressure, the residual solid tin in the cavities has a higher melting temperature compared to bulk tin. When the overheating is not large enough, the residual solid tin in the cavities regrows towards the inner part of the droplet. As soon as the inner edge of the oxide layer, i.e. the mouth of the cavity, is reached it acts as a nucleus for the bulk tin. This process effectively decreases the obtained undercooling. With increasing overheating, the regrowth distance becomes larger. Then it takes more time to grow and to form a nucleus. Consequently the undercooling increases. Finally, when the overheating is larger than a critical value, the residual solid tin in the cavities disappears. As a result, the

common bulk and surface nucleation behavior dominates as mentioned above (See Papers 1 and 2). Generally speaking, this nucleation process is a competition between the amount of the residual tin crystal in the cavities and its regrowth rate related to the cavity size distribution and cooling rate. Finally, in Paper 4 the size of cavities  $r_c$  was estimated from the obtained undercooling based on the modified model.

In summary, in this thesis there are three achievements listed as follows:

- (i) The crystal nucleation of single micro-sized tin droplets were investigated by in-situ measurements by DFSC during rapid heating-cooling processes at rates up to  $4 \times 10^4$  K/s. The cooling rate, droplet size and overheating effects on crystal nucleation were investigated experimentally. (Papers 1-4)
- (ii) For the first time the issue of separating the mutual effects of droplet size and cooling rate in rapid solidification has been solved. (Papers 1 and 2)
- (iii) In a first attempt a theoretical model was developed on the basis of the classical heterogeneous nucleation theory and supplemented by the cavity induced heterogeneous nucleation model and cavity size dependent growth. It allows to describe the cooling rate, droplet size and prior liquid overheating dependences on crystal nucleation in single micro-sized tin droplets. (Papers 3 and 4)

Finally, the in-situ DFSC measurements during rapid cooling and the new developed theoretical model are believed to be able to direct further research to shed more light on the nucleation processes for metallic droplet solidification and related rapid solidification processes also beyond the particular system analyzed in this thesis.

## 1.6. Prospective research directions

In the field of metallic materials, metal droplets and metallic glasses are two classes which attract more attentions because of their wide use as functional and structure materials. Metallic glasses with a glass-like structure, the new kind of metal materials, have attracted special attention in terms of both fundamental understanding and attractive potential applications [76-78]. In this thesis, the crystal nucleation of single micro-sized metal droplets in rapid solidification was investigated. But there are still some important open questions on metallic glasses which could be investigated further by applying the developed experimental and theoretical tools in this thesis.

Usually, the new classes of metallic glasses are closely related to two important fundamental issues: (i) avoidance of crystallization upon cooling of the liquid and (ii) control of crystallization upon heating of the glass. Both these two aspects involve kinetic competition between the nucleation and growth of metastable and stable crystalline phases. While the critical cooling rate (CCR) that represents the minimum cooling rate to bypass the nose of the time-temperature transformation (TTT) curve for the onset of nucleation during cooling is usually reported as a specific value [79], other work has shown that there is in reality a CCR range that should be considered in glass formation [80, 81]. The examination of the crystallization kinetics upon heating is often based upon a Johnson-Mehl-Avrami-Kolmogorov (JMAK) analysis [82], that is evaluated from isothermal or continuous heating measurements at temperatures near the glass transition temperature  $T_g$ . Though this type of kinetics analysis is convenient, it is necessary to extrapolate the analysis results to high temperatures in order to evaluate the CCR range. Since glass formation develops at high liquid undercooling and the crystallization kinetics measurements are restricted to heating experiments and with a limited temperature range not far above  $T_g$ , the extrapolations must be carried out over a rather wide



temperature range. Due to the wide range of cooling rates of DFSC, the direct measurements of critical cooling rate ranges of metallic glasses during rapid quenching are now accessible and can be used to confirm the stochastic nature of crystal nucleation behavior and its influence on glass formation. These results will provide useful input for kinetic analysis. Moreover, the measurements can also be done either isothermally (holding at specific temperature for long time) or non-isothermally (upon heating or cooling at different rates to temperatures near the onset temperature of crystallization). Then according to these experimental results, the kinetic competition between the nucleation and growth of metastable and stable crystalline phases in metallic glass formers can be analyzed.

In summary, DFSC opens up a new field to reveal nucleation and phase transition kinetics in metallic samples, making it possible to validate theoretical estimation by experimental results.

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## ***Chapter 2 Publications***

## **2.1. Cooling rate dependence of undercooling of pure Sn single drop by fast scanning calorimetry**

Applied Physics A, 2011, 104(1): 189-196

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### **Author contributions**

<b>B. Yang</b>	Preparation of the manuscript, DFSC measurements and experimental data analysis.
<b>Y. Gao, C. Zou and Q. Zhai</b>	Preparation of the Sn droplets.
<b>A. S. Abyzov and J. W. P. Schmelzer</b>	Development of the theoretical model and calculations.
<b>E. Zhuravlev</b>	Improvement of and help with differential fast scanning calorimetry.
<b>C. Schick</b>	Supervision of the research.

## **2.2. Size and rate dependence of crystal nucleation in single tin drops by fast scanning calorimetry**

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### **Author contributions**

<b>B. Yang</b>	Preparation of the manuscript, DFSC measurements and experimental data analysis and theoretical calculations.
<b>A. S. Abyzov and J. W. P. Schmelzer</b>	Development of the theoretical model and calculations.
<b>E. Zhuravlev</b>	Improvement of and help with differential fast scanning calorimetry.
<b>Y. Gao</b>	Preparation of the Sn droplets.
<b>C. Schick</b>	Supervision of the research.



### **2.3. Undercooling dependence on liquid overheating by differential fast scanning calorimetry**

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#### **Author contributions**

<b>B. Yang</b>	Preparation of the manuscript, DFSC measurements and experimental data analysis.
<b>J. Perepezko</b>	Development of the theoretical model.
<b>E. Zhuravlev</b>	Improvement of and help with differential fast scanning calorimetry.
<b>Y. Gao</b>	Preparation of the Sn droplets.
<b>C. Schick</b>	Supervision of the research.

## **2.4. Dependence of crystal nucleation on prior liquid overheating by differential fast scanning calorimeter**

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### **Author contributions**

<b>B. Yang</b>	Preparation of the manuscript, DFSC measurements and experimental data analysis and theoretical calculations.
<b>J. Perepezko and J. W. P. Schmelzer</b>	Development of the theoretical model.
<b>Y. Gao</b>	Preparation of the Sn droplets.
<b>C. Schick</b>	Supervision of the research.

## List of Contributions

### Publications

1. Y. Gao, E. Zhuravlev, C. Zou, **B. Yang**, Q. Zhai and C. Schick. *Calorimetric measurements of undercooling in single micron sized SnAgCu particles in a wide range of cooling rates*. Thermochim Acta, 2009. 482(1-2): 1-7.
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3. **B. Yang**, Y. Gao, C. Zou, Q. Zhai, E. Zhuravlev and C. Schick. *Repeated nucleation in an undercooled tin droplet by fast scanning calorimetry*. Mater Lett, 2009. 63(28): 2476-8.
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2. **B. Yang**, A. S. Abyzov, E. Zhuravlev, J. W. P. Schmelzer and C. Schick, “Nucleation of pure Sn single particle by fast scanning calorimetry - experimental part”. Lecture, 16<sup>th</sup>

- Research Workshop Nucleation Theory and Applications, April 14<sup>th</sup> - 22<sup>nd</sup>, 2012 Dubna, Russia
3. **B. Yang**, A. S. Abyzov, E. Zhuravlev, Y. Gao, J. W. P. Schmelzer and C. Schick, “Cooling rate dependence of undercooling of pure Sn single partially molten drop by fast scanning calorimetry”. Poster, 12<sup>th</sup> Lahnwitzseminar on Calorimetry, June 10<sup>th</sup> - 15<sup>th</sup>, 2012 Rostock, Germany
  4. **B. Yang**, A. S. Abyzov, E. Zhuravlev, Y. Gao, J. W. P. Schmelzer and C. Schick, “Effect of melt overheating and cooling rate on undercooling of pure Sn single particle”. Poster, 12<sup>th</sup> Lahnwitzseminar on Calorimetry, June 10<sup>th</sup> - 15<sup>th</sup>, 2012 Rostock, Germany
  5. **B. Yang**, A. S. Abyzov, E. Zhuravlev, Y. Gao, J. W. P. Schmelzer and C. Schick, “Size dependent nucleation of single tin particles by differential fast scanning calorimetry”. Lecture, The Minerals, Metals & Materials Society 142<sup>nd</sup> Annual Meeting & Exhibition, March 3<sup>rd</sup> - 7<sup>th</sup>, 2013 San Antonio, Texas, USA
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  7. **B. Yang** and C. Schick, “Nucleation of single Sn droplet by fast scanning calorimetry”. Lecture, 17<sup>th</sup> Research Workshop Nucleation Theory and Applications, April 13<sup>rd</sup> - 21<sup>st</sup>, 2013 Dubna, Russia
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12. **B. Yang**, Y. Gao and C. Schick, “Crystallization kinetics and glass transition of AlNiYCoLa metallic glass by differential fast scanning calorimeter”. Poster, 13<sup>th</sup> Lahnwitzseminar on Calorimetry, June 15<sup>th</sup> - 20<sup>th</sup>, 2014 Rostock, Germany
13. **B. Yang**, Y. Gao and C. Schick, “Non-isothermal crystallization kinetics and fragility of Al<sub>86</sub>Ni<sub>6</sub>Y<sub>4.5</sub>Co<sub>2</sub>La<sub>1.5</sub> metallic glass by differential fast scanning calorimetry”. Lecture, The 11<sup>th</sup> European Symposium on Thermal Analysis and Calorimetry, August 17<sup>th</sup> - 21<sup>st</sup>, 2014 Espoo, Finland
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## **Appendix**

### **A1      Calorimetric measurements of undercooling in single micron sized SnAgCu particles in a wide range of cooling rates**

Thermochimica Acta, 2009. 482(1-2): 1-7

DOI: <http://dx.doi.org/10.1016/j.tca.2008.10.002>

In this paper, the undercooling of one single micron sized droplet was successfully measured in-situ by a differential fast scanning calorimeter firstly by us. The experimental details of single micro-sized droplets measurements, such as calibration, heat transfer limitations and sample placement on the sensor, were carefully discussed, which are the basis of the research in this thesis.

## **A2      Repeated nucleation in an undercooled tin droplet by fast scanning calorimetry**

Materials Letters, 2009. 63(28): 2476-2478

DOI: <http://dx.doi.org/10.1016/j.matlet.2009.08.041>

In this paper, the undercooling of one single micro-sized tin droplet was measured at a cooling rate of  $10^4$  K/s by the differential fast scanning calorimeter and the repeated (1000 melting-solidification cycles) nucleation mechanism was discussed by a statistic method. We found that a single nucleation mechanism model was capable of describing the nucleation process at a high cooling rate. It means that the nucleation mechanism didn't change even for 1000 melting-solidification cycles at one cooling rate, which is the basis of the research in this thesis.

## **Erklärung**

Ich versichere hiermit an Eides statt, dass ich die vorliegende Arbeit selbstständig angefertigt und ohne fremde Hilfe verfasst habe, keine außer den von mir angegebenen Hilfsmitteln und Quellen dazu verwendet habe und die den benutzten Werken inhaltlich und wörtlich entnommenen Stellen als solche kenntlich gemacht habe.

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