Kinetic study on eutectic reaction between boron carbide and stainless steel by differential thermal analysis

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Abstract
In a postulated severe accidental condition of sodium-cooled fast reactor (SFR), the eutectic reaction between boron carbide (B₄C) as control rod element and stainless steel (SS) as control rod cladding or related structure materials may take place. Thus, the kinetic behavior of the B₄C–SS eutectic reaction is one of the important phenomena to be considered when evaluating the core disruptive accidents in SFR. In this study, for the first step to obtain the fundamental information on kinetic feature of the B₄C–SS eutectic reaction and compare the pervious findings, the thermal analysis using the pellet samples of B₄C and Type 316L SS as a different experimental approach was performed up to 1773 K at different heating rates of 2.5-10 K min⁻¹. The differential thermal analysis (DTA) endothermic peaks for the B₄C–SS eutectic reaction appeared from 1483K to 1534K and systematically shifted to higher temperatures with increasing heating rate. Based on this kinetic feature, apparent activation energy and pre-exponential factor for the B₄C–SS eutectic reaction were determined by Kissinger method. It was found that the kinetic parameters obtained by thermal analysis were comparable to the literature values of the thinning experiment at high temperatures. In addition, the microstructure and element distribution formed in the interdiffusion layer composed of the B₄C–SS system were analyzed by the electron probe microanalyzer (EPMA), which can provide key validation data on elemental interdiffusion behavior in the early stage of the eutectic reaction for reflecting the reaction kinetic modeling.

Keywords : Sodium-cooled fast reactor, Severe accident, Eutectic reaction, Kinetic behavior, Thermal analysis, Rate constant

1. Introduction
In a postulated severe accidental condition of sodium-cooled fast reactor (SFR), the eutectic reaction between boron carbide (B₄C) as control rod element and stainless steel (SS) as control rod cladding or related structure materials may take place before the fuel rods melt. The B₄C–SS eutectic reaction may cause loss of control rod elements in the early stage of severe accident and negative effect of core melting process. Thus, the behavior of the B₄C–SS eutectic reaction is one of the important phenomena to be considered when evaluating the core disruptive accidents in SFR (Yamano, et al., 2019).

In the past, many experimental studies of the B₄C–SS eutectic reaction have been carried out in the field of light water reactor safety (Nagase, et al., 1997) (Hofmann, et al., 1990) (Shibata, et al., 2015). However, it is not sufficient to evaluate the eutectic reaction progress due to heterogeneous reaction feature. Besides, kinetic information on the B₄C–SS eutectic reaction is limited due to difficulty of in-situ measurement at high temperatures. Nagase, et al. (Nagase, et al., 1997) investigated the reaction kinetics and presented the reaction rate, which is based on the thickness of the eutectic reaction layer and duration time after the thinning experiment for the B₄C–SS eutectic reaction. Though the findings and knowledge obtained in the thinning experiment are not based on the results of in-situ measurement for the eutectic
reaction progress, the following equations on reaction rate constant currently are used for severe accident analysis code for the light water reactor safety.

\[ K_{\text{low}}(m^2s^{-1}) = 1.49 \times 10^{-2} \exp\left(-\frac{250000}{RT}\right) \quad 1073K \leq T \leq 1473K \]  

\[ K_{\text{high}}(m^2s^{-1}) = 1.40 \times 10^{10} \exp\left(-\frac{549000}{RT}\right) \quad 1498K \leq T \leq 1623K \]  

In this study, we tried to evaluate the rate constant of the B₄C–SS eutectic reaction by using thermal analysis technique as a different experimental approach. For the first step, viability of thermal analysis was confirmed through the preliminary experiment for the applicability of the sample crucible. And then, based on the peaks of differential thermal analysis (DTA) curves at different heating rates, kinetic parameters such as apparent activation energy and pre-exponential factor were estimated by Kissinger method (Kissinger, 1957) as a law of chemical reaction kinetics. After that, the Arrhenius type rate constant based on the kinetic parameters by DTA was discussed and compared with the literature value in the previous thinning experiment. For post analysis of the sample after the DTA measurement, the interdiffusion layer structure formed at the B₄C-SS eutectic reaction interface was investigated by the electron probe microanalyzer (EPMA) to understand the elemental interdiffusion behavior in the early stage of the reaction for reflecting the reaction kinetic modeling.

Nomenclature

\( A \): Pre-exponential factor, [s⁻¹]
\( E \): Energy, [kJ mol⁻¹]
\( K \): Rate constant, [m² s⁻¹]
\( R \): Gas constant, [kJ mol⁻¹ K⁻¹]
\( S \): Surface area, [m²]
\( T \): Temperature, [K]
\( \beta \): Heating rate, [K s⁻¹]
\( k \): First order rate constant, [s⁻¹]

Subscripts

\( a \): Activation
\( high \): high temperature range
\( low \): low temperature range
\( p \): Peak top of the DTA curve
\( B4C-SS \): B₄C–SS eutectic reaction

2. Experimental

2.1 DTA measurement

DTA measurements were carried out using SETSYS Evolution 24 (SETARAM) of TG-DTA equipment under a 100 mL min⁻¹ argon (Ar) flow as a carrier gas, in Tungsten (W) / Rhenium (Re) detector. The samples of B₄C and/or SS can be heated up to the desired temperatures with graphite heater. The details of the experimental apparatus have been reported previously (Kikuchi, et al., 2013). DTA curves were recorded by using the software SETSOFT 2000 with data sampling rate of 1 point s⁻¹.

Chemical reagents of Type 316 L SS (150μm in particle size, Kojundo Chemical) and B₄C (150μm in particle size, Kojundo Chemical) were used without further purification and weighed in approximately 50 mg and 25 mg, respectively. All sample powders were mechanically pressed to make pellet samples with height of approximately 1 mm for Type 316 L SS and approximately 2 mm for B₄C as shown in Fig. 1. These samples without sintering were placed into the DTA sample crucible (4 mm in inner diameter and 7.5 mm in depth). In this study, graphite and alumina crucibles (Fig. 2) were
used because these crucibles were widely used for B$_4$C/SS sample in many experimental works (Zhang, et al., 2008) (Chang, et al., 2007) (Goldstein, et al., 2001) (Kim, et al., 2000).

In order to track the thermal behavior of the B$_4$C–SS eutectic reaction, the DTA measurement at high temperatures is needed because the cited reaction onset is around 1500 K (Nagase, et al., 1997). Thus, correction experiment was performed to secure the accuracy of measurement at desired high temperatures. A temperature correction using standard materials is indispensable to minimize the significant measurement uncertainty. Au (m.p.:1337 K) and Ni (m.p.:1728 K) as a standard material were used for high temperature range correction in addition to In (m.p.:430 K), Pb (m.p.:600 K), and Al (m.p.:933 K) for low temperature range. The measurement deviation became less than one percent by temperature correction experiment. After its temperature correction, the DTA measurements were carried out and reproducibility was confirmed.

The preliminary experiment was performed to confirm the thermal behavior of each pure sample such as Type 316 L SS melting and the reactivity against the sample crucibles. Each pellet sample was heated from 300 K to 1773 K at a heating rate of 10 K min$^{-1}$. Based on the results of the preliminary experiments, applicability of the DTA crucibles was confirmed.

On the other hand, with regard to the B$_4$C–SS eutectic reaction experiment, two cases of sample set as shown in Fig. 3 were prepared to investigate the influence of sample position. The DTA measurements for the pellet samples of B$_4$C-Type 316 L SS were carried out from 300 K to 1773 K at different heating rates of 2.5, 5 and 10 K min$^{-1}$ (Table 1). Besides, all samples were cooled to room temperature at cooling rate of 20 K min$^{-1}$. Based on the peaks of DTA curves at different heating rates, the kinetic parameters were estimated by using Kissinger method to compare with the literature values in the previous work.

![fabrication procedure and appearance of samples](image1.png)

(a) Fabrication procedure for pellet samples                            (b) Appearance of pellet samples

Fig. 1 Preparation for pellet samples.

![crucible images](image2.png)

(a) Graphite crucible                                             (b) Alumina crucible

Fig. 2 Appearance of DTA sample crucibles.
2.2 Analysis of reaction product

The coupled pellet samples of B₄C-Type 316 L SS after the DTA measurements were sectioned perpendicularly. The cross-sections embedded in the epoxy resin were ground and polished metallographically and then examined by optical microscope (VHX-5000, Keyence) and EPMA (JXA-8230, JEOL) to investigate the microstructure and element distribution throughout the sample. The sample surface was coated with carbon to increase conductivity for EPMA measurement. Backscattered-electron (BSE) and mapping images were acquired using an accelerating voltage of 15 kV and a probe current of 10⁻⁶ to 10⁻⁷ A. The K-lines for Fe, Cr, Ni, Mo, B and C were applied for element mapping and quantitative analysis.

3. Results and Discussion

3.1 Preliminary experiment

Figures 4 and 5 show DTA curves for pure Type 316L SS pellet and B₄C pellet samples with the temperature range of 700-1773 K at a heating rate of 10 K min⁻¹. In case of alumina crucible, the single sharp endothermic peak at around 1700 K was apparently identified as SS melting in Fig. 4(a). Besides, there is no outstanding thermal change except SS melting. Moreover, the DTA measurement for pure B₄C pellet sample using alumina crucible was also performed and there is no thermal change related to the reaction as shown in Fig. 4(b). Thus, this indicates that alumina crucible is applicable for B₄C/SS sample.
On the other hand, though no thermal change of DTA curve for B\textsubscript{4}C pellet sample appeared (Fig. 5(b)), some endothermic peaks of the DTA curve for Type 316L SS pellet sample were identified at around 1500 K in case of graphite crucible (Fig. 5(a)), which is apparently low temperature in comparison with the SS melting in case of alumina crucible as shown in Fig. 4(a). It was considered that some reactions between the sample and the graphite crucible might occur because the DTA endothermic peak shape shows the multi-step reaction feature. Though the product analysis after the DTA measurement was not carried out, it was suspected that one of the reactions might be the eutectic reaction between carbon (C) of graphite crucible and iron (Fe) of SS because the onset point of endothermic peak is close to eutectic temperature of the Fe-C system (Chipman, 1972). Thus, it is not practical to use the graphite crucible for the B\textsubscript{4}C–SS eutectic reaction though these were widely used in many experimental works (Zhang, et al., 2008) (Chang, et al., 2007) (Goldstein, et al., 2001) (Kim, et al., 2000).

3.2 B\textsubscript{4}C–SS eutectic reaction experiment

The DTA measurements for two sample sets of B\textsubscript{4}C–type 316 L SS pellet were performed to confirm the detectability because the temperature sensor of DTA is located near the bottom of the sample crucible. As described in Fig. 3, the SS pellet was put on the B\textsubscript{4}C pellet into the sample crucible to contact each other without further pressing in Case 1. On the other hand, position of SS and B\textsubscript{4}C pellet samples in Case 2 is opposite of Case 1. Figure 6 shows the DTA curves for B\textsubscript{4}C–type 316L SS pellet samples heated up to 1580 K at different heating rates of 2.5, 5 and 10 K min\textsuperscript{-1}. In both Cases 1 and 2, the DTA curves show the endothermic feature as the B\textsubscript{4}C–SS eutectic reaction. Besides, multi-step reaction

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Fig. 4 DTA curves for pure pellet samples placed into alumina crucible at a heating rate of 10 K min\textsuperscript{-1}.

(a) DTA curve for Type 316L SS pellet sample  
(b) DTA curve for B\textsubscript{4}C pellet sample

Fig. 5 DTA curves for pure pellet samples placed into graphite crucible at a heating rate of 10 K min\textsuperscript{-1}.

(a) DTA curve for Type 316L SS pellet sample  
(b) DTA curve for B\textsubscript{4}C pellet sample
feature and systematic endothermic peak shift with increasing heating rate appeared from 1483K to 1534K. However, peak shape in Case 1 is broad and vague in comparison with that in Case 2 because of DTA sensibility. Thus, clear and sharp endothermic peak data obtained in Case 2 is practically useful for kinetic evaluation.

The DTA curve at a heating rate of 2.5 K min⁻¹ in Case 2 appeared two endothermic reaction region as multi-step reaction feature at approximately 1483 and 1505 K, respectively (Fig. 6(b)). In order to clarify the onset temperature of the eutectic reaction, the B₄C–type 316L SS pellet sample was heated up to around the onset temperature of approximately 1483 K at a heating rate of 2.5 K min⁻¹. Figure 7 shows the DTA curves for B₄C–type 316L SS pellet samples heated up to around the reaction onset at a heating rate of 2.5 K min⁻¹ and appearances of the contact surface in the samples after the DTA measurements. In case of Run 1, the sample heated up to 1495 K was partially melt and endothermic peak was 1483 K, which is consistent with that of Case 2 (Fig. 6(b)).

On the other hand, the surface of B₄C and type 316L SS pellet samples in case of Run 2 did not stick each other from the appearance of the samples after the DTA measurement (Fig. 7). Besides, there is no thermal change below this temperature in case of Run 2 from DTA curve. Thus, the first endothermic peak of approximately 1483 K at a heating rate of 2.5 K min⁻¹ in Case 2 (Fig. 6(b)) can be the onset temperature of the eutectic reaction for kinetic consideration.

The first endothermic peak top temperature of the DTA curves in Case 2 obtained in five times measurement at each heating rate were summarized in Table 2. Though the DTA curves include multi-step reaction feature, the first endothermic peak was recognized as onset temperature of the eutectic reaction. Based on this consideration, it is possible to evaluate the kinetics for the early stage of the B₄C–SS eutectic reaction.

![Fig. 6 DTA curves for B₄C–type 316 L SS pellet samples heated up to 1580 K at different heating rates.](image-url)
Fig. 7 DTA curves for B$_4$C–type 316 L SS pellet samples heated up to around the onset temperature of the eutectic reaction at a heating rate of 2.5 K min$^{-1}$ and appearances of the samples after DTA measurements.

3.3 Interdiffusion layer formed in the B$_4$C-SS system

As illustrated in Fig. 6, the DTA measurements in Cases 1 and 2 were performed at the different sample position and heating rates to discuss the DTA sensibility. The cross section of the B$_4$C–type 316 L SS pellet samples cooled to room temperature at a cooling rate of 20 K min$^{-1}$ after the DTA measurements was analyzed by EPMA to provide the helpful information for elucidating the mechanism in the early stage of the B$_4$C-SS eutectic reaction and the reaction kinetic modeling.

Figures 8 and 9 show the appearance, cross-sectional BSE image and element mapping for the B$_4$C–type 316 L SS pellet samples after the DTA measurement heated up to 1573 K at a heating rate of 10 K min$^{-1}$ in Cases 1 and 2, respectively. In Case 1 shown in Fig. 8, the SS located at the top lost its original shape completely and was deformed to wrap around a part of the B$_4$C pellet at the bottom. In Case 2 shown in Fig. 9, the SS at the bottom completely lost its original shape and was deformed to wrap around the B$_4$C pellet partially at the top. As a result of interdiffusion between both constituents, three types of layer structure were formed in each sample (hereafter, referred to as Layer I, II, and III from the outside). Element mapping image shows that the Layer I was mainly composed of SS component elements and a small amount of boron and carbon. It was also shown that concentrated Cr and carbon accumulated in Layer II, and Ni at the boundary between Layers II and III.

<table>
<thead>
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<th>Heating Rate</th>
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<tbody>
<tr>
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<td>1502.2</td>
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<tr>
<td>10 K min$^{-1}$</td>
<td>1534.3</td>
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<tr>
<td>5 K min$^{-1}$</td>
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<tr>
<td>10 K min$^{-1}$</td>
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<tr>
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<td>10 K min$^{-1}$</td>
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<td>1526.6</td>
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The microstructure formed in areas X and Y of Layer I and area Z of Layer II shown in Fig. 8(b) are represented in Fig. 10. From the results of the quantitative analysis, it is expected that eutectic structure composed of Fe₃C and Fe₇C₃ type compounds was formed in the Layer I, in addition to the FeB type compound existing as a solid phase at high temperature. As minor phases, (Fe,Mo)₃B₂ type compound and graphite are also expected to be formed in the Layer I as seen in Fig. 10(a) and (b). For Layer II, in which a width of approximately 100 µm was evenly formed between Layers I and III, it is expected that the microstructure consisting of a mixture of CrB and FeB phases was formed, as shown in Fig. 10(c). Based on the phase diagram of the B-Cr-Fe system (Yamada et al., 2008), it is probable that both phases were solid at the time of the DTA measurements. In Fig. 10(c), carbon-rich phases of (Fe,Cr,Ni)(C,B) and graphite were also formed in the Layer II, which are considered to correspond to the concentrated phases of carbon shown in Figs. 8-9. In the Layer III, no significant precipitates were formed in the B₄C pellet. Figure 11, however, reveals that limited amount of the SS constituent elements diffused into the B₄C pellet in the order of Fe> Ni> Cr> Mo, which was provided by a line scan analysis using an electron probe with a diameter of 10 µm in 5 µm steps in the direction perpendicular to the Layer II / III interface. Considering that the concentration of Ni in SS is less than 1/6 of Fe, it is suggested that Ni tends to diffuse preferentially to the solid B₄C pellet as much as Fe. Regarding the diffusion of boron to the original SS side, the concentration of boron tends to decrease monotonically and drastically from the position in the solid B₄C pellet about 500 µm away from the Layer II / III interface, as shown in Fig. 11.

Figure 12 shows the appearance, cross-sectional BSE image and element mapping for the samples heated up to 1573 K at a heating rate of 2.5 K min⁻¹ in Case 2. It is seen that the melt fully covered the B₄C pellet. The melt coverage is higher than the samples shown in Figs. 8 and 9. It is speculated that this is because slow heating rates promote long-term interdiffusion at high temperatures between the coupled samples. However, three types of layer structure formed in the cross section are very similar between the tests shown in Figs. 8, 9 and 12.

From the fact that B₄C pellet was reduced by 250-400 µm in thickness from the initial interface as seen in Fig. 8(b), it is estimated that a significant amount of boron and carbon derived from B₄C pellet rapidly diffuse to the outermost surface of SS to form a eutectic melt containing the SS constituent element. The melt partially or fully wrapped the B₄C pellet due to its low viscosity properties.

Fig. 8 Appearance, cross-sectional BSE image, and element mapping for the B₄C–type 316 L SS pellet sample after DTA measurement heated up to 1573 K at a heating rate of 10 K min⁻¹ (Case 1).
Fig. 9 Appearance, cross-sectional BSE image, and element mapping for the B₄C–type 316 L SS pellet sample after DTA measurement heated up to 1573 K at a heating rate of 10 K min⁻¹ (Case 2).

Fig. 10 Microstructure formed in areas X and Y of Layer I and area Z of Layer II shown in Fig. 8(b).
Fig. 11 Concentration profile at the interface of Layers II / III around area Z shown in Fig. 8.

Fig. 12 Appearance, cross-sectional BSE image and element mapping for the B$_4$C–type 316 L SS pellet sample after DTA measurement heated up to 1573 K at a heating rate of 2.5 K min$^{-1}$ (Case 2).
3.4 Kinetic consideration

Kinetic approach to the B₄C–SS eutectic reaction was challenged by focusing on the DTA endothermic peaks because the DTA curves include multi-step reaction feature as mentioned before. However, from DTA measurements and the observation of the samples after the DTA measurements, the first endothermic peaks could be identified as an onset temperature of the B₄C–SS eutectic reaction as shown in Table 2. Thus, the apparent activation energy \( E_a \) and pre-exponential factor \( A \) as Arrhenius kinetic parameters for the early stage of the B₄C–SS eutectic reaction can be estimated by the Kissinger method (Kissinger, 1957).

Figure 13 shows the Kissinger plot for the eutectic reaction of B₄C–Type 316L SS pellet samples with the temperature range of 1483-1534 K at heating rates of 2.5, 5 and 10 K min⁻¹. We used the least squares method for approximation of this plot. Based on the liner plot, the apparent activation energy \( E_a \) and pre-exponential factor \( \ln A \) were 511 ± 119 kJ mol⁻¹ and 34.6 ± 9.7 s⁻¹, respectively. Thus, the first-order of Arrhenius type rate constant is expressed as follows;

\[
k_{B4C-SS}(s^{-1}) = 1.11 \times 10^{15} \exp\left(-\frac{511000}{RT}\right) \quad 1483K \leq T \leq 1534K
\]  

(3)

Fig. 13 Kissinger plot for the eutectic reaction of B₄C–Type 316L SS pellet samples.

Some experimental works on the rate constant for the B₄C–SS eutectic reaction were reported in the field of light water reactor safety. Nagase et al. (Nagase, et al., 1997) presented the rate constant obtained from the thickness of the eutectic reaction layer of B₄C-Type 304 SS in the thinning experiment as shown in Eqs. (1) and (2). Each equation has different applicable temperature range such as low temperature range for Eq. (1) and high temperature range for Eq. (2). Though the rate constant obtained by thermal analysis is the first-order, we tried to compare the previous findings. In addition, the previous findings in the thinning experiment using Type 304 SS was used as reference for comparative consideration due to lack of knowledge of Type 316L SS. Considering the eutectic melt initially formed on the SS side as shown in Fig. 8, it could be assumed that the diffusion of the SS constituent elements would advance toward the surface of B₄C pellet with diameter of 3 mm as shown in Fig. 14, which is evident from EPMA mapping of interdiffusion layer structure formed in the interface of the B₄C-SS eutectic reaction. Based on this assumption, rate constant could be expressed by Eq. (4).

\[
K_{B4C-SS}(m^2s^{-1}) = \frac{S(m^2)}{k_{B4C-SS}(s^{-1})}
\]

(4)

where \( S \) is the surface area of B₄C pellet.

Then, from Eq. (4), rate constant is obtained as follows;

\[
K_{B4C-SS}(m^2s^{-1}) = 7.85 \times 10^{9} \exp\left(-\frac{511000}{RT}\right) \quad 1483K \leq T \leq 1534K
\]  

(5)
Figure 15 shows the comparison of the rate constants for the B₄C–SS eutectic reaction with temperature dependence in cases of the present thermal analysis and the previous thinning experiment. The rate constant at high temperatures in the present study is slightly larger than that of the previous thinning experiment because Kissinger method is a kinetic law for estimating the maximum rate constant in the early stage of the reaction. However, this slight difference is acceptable level when considering the uncertainty of DTA measurement. Thus, it was interpreted that rate constant based on the thermal analysis in Eq. (5) was comparable to the value of the Eq. (2) in the previous work.

4. Conclusion

In this study, differential thermal analysis (DTA) as a different experimental approach was employed to investigate the kinetics of the B₄C–SS eutectic reaction and to compare the previous findings in the conventional thinning experiment. It was revealed that alumina crucible for the DTA measurement was more suitable for the B₄C–SS eutectic reaction than graphite one though both crucibles were widely used for B₄C/SS sample in many experimental works.

In case of the DTA measurement at lower heating rate, multi-step reaction feature of the B₄C–SS eutectic reaction appeared significantly. It was confirmed that the first endothermic peak of the multi-step reaction was identified as an onset temperature of the eutectic reaction through the DTA measurements and observation of the sample after the DTA measurement. Besides, from the appearance of samples after the DTA measurements, it was revealed that the eutectic
melt was initially formed on the SS side and covered the surface of the B4C pellet. Moreover, it was revealed that the interdiffusion layers in the early stage of the B4C–SS eutectic reaction were identified, which is evident from the EPMA analyses for the microstructure and element distribution of the cross section for each sample.

Based on the first endothermic peaks measured at different heating rates, the first-order Arrhenius type rate constant and these related kinetic parameters for the early stage of the B4C–SS eutectic reaction were determined by Kissinger method. The rate constant based on the advancement of SS diffusion toward the surface of the B4C pellet assumed by the DTA measurements and their post analyses were comparable to the literature values at high temperatures in the previous thinning experiment.

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