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ARTICLE

Reaction Behavior between Sodium and Molten Salt caused by the Heat Transfer Tube Failure for Sodium-Cooled Fast Reactor Coupled to Thermal Energy Storage System

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In a sodium-cooled fast reactor (SFR) coupled to thermal energy storage (TES) system, the reaction between nitrate molten salt as thermal energy storage medium and sodium (Na) as reactor coolant might occur under postulated accidental conditions. Thus, the reaction behavior of Na-nitrate molten salt is one of the important phenomena in terms of safety assessment of the SFR with TES system. In this study, for the first step, the thermal analyses using sodium nitrate ($NaNO_3$), potassium nitrate (KNO_3) and $NaNO_3$-KNO_3 were performed as preliminary tests. Besides, reaction experiments on Na-$NaNO_3$ and Na-KNO_3 were performed to obtain the fundamental information for Na-solar salt reaction. And then, the reaction experiment on Na-solar salt was performed. It was found that Na-solar salt reaction occurred after the $NaNO_3$-KNO_3 eutectic melting. It was confirmed that the sharp exothermic peak with thermal runaway feature appeared in case of first heating of Na-$NaNO_3$-KNO_3 mixture as reported in the previous study. Moreover, it was revealed that the broad exothermic peak for Na-solar salt was successfully obtained in case of second heated $NaNO_3$-KNO_3 mixture (solar salt) with Na. Based on the measured reaction temperature, the kinetic parameters and rate constant were obtained and compared with the sodium-water reaction.

KEYWORDS: sodium-cooled fast reactor, nitrate molten salt, reaction behavior, thermal analysis, heat transfer tube failure

I. Introduction

In a sodium-cooled fast reactor (SFR) coupled to thermal energy storage (TES) system, nitrate molten salt known as “solar salt” mixture with a mass percentage of 60% sodium nitrate ($NaNO_3$) and 40% potassium nitrate (KNO_3) is the most promising candidate as a thermal energy storage medium because it is deployed in a solar thermal power generation business.[1] The SFR with TES needs a heat exchanger between sodium (Na) and molten salt. Under a postulated accidental condition of heat transfer tube failure in the heat exchanger, the reaction between nitrate molten salt and Na might occur. Thus, the reaction behavior of Na-nitrate molten salt is one of the important phenomena in terms of safety assessment of the SFR with TES system. Many experimental studies on the thermal behavior of nitrate molten salts such as $NaNO_3$ and KNO_3 have been carried out previously.[2,3] However, the reaction data of nitrate molten salts with Na is limited because the only qualitative evaluation was reported in the previous study.[4] There is no sufficient information that contributes to the safety design and safety evaluation of SFR with TES system.

The objective of this study is to clarify reaction behavior of Na-nitrate molten salt caused by the heat transfer tube failure. In this paper, the first step is thermal analyses using individual nitrate molten salt reagents to obtain the fundamental information as preliminary tests for sodium-nitrate molten salt reaction experiment. The second step is the reaction experiments on Na-$NaNO_3$ and Na-KNO_3 to obtain the fundamental information on each reaction feature for Na-solar salt reaction. The third step is the reaction experiment on Na-solar salt to compare with the previous findings and discuss the obtained results. Based on the reaction temperature at different heating rate, this study estimates kinetic parameters and rate constant by using kinetic method.[4]

II. Experimental

For the thermal analysis, the differential scanning calorimetry (DSC-111, SETARAM) installed in the glove box in an argon (Ar) atmosphere was used. Considering the findings of previous studies on nitrate molten salts and the reactivity of Na, upper open sample crucibles made of a stainless steel (Type 304L, 5 mm in diameter × 76 mm in depth) were used for DSC measurements.[2,5] Experimental conditions are summarized in **Table 1**. Alumina (α-Al_2O_3) powder with a high melting point (99 mass%, KANTO CHEMICAL CO., INC.) was added to the crucible placed in the reference side. Chemical reagent of $NaNO_3$ granule (approximately 1 mm in granule size, 99 mass%, FUJIFILM Wako Pure Chemical Corporation) and KNO_3 granule (approximately 0.8 mm in granule size, 99 mass%, FUJIFILM Wako Pure Chemical Corporation) were used without further purification and shape forming and weighed in approximately 50 mg (**Fig. 1**). Solar salt was prepared by weighing approximately 30 mg of $NaNO_3$ and 20 mg of KNO_3 based on the mass percentage of 60% $NaNO_3$ and 40% KNO_3, and placed in the sample crucible. $NaNO_3$ granule was placed

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*Corresponding author, E-mail: sato.rika@jaea.go.jp under KNO_3 granule in contact with each other without further mixing and heat-treatment. At first, in order to obtain the fundamental information on the thermal behavior of KNO_3, $NaNO_3$ and $NaNO_3$-KNO_3 mixture based on the mass fraction of solar salt, the preliminary experiment using each nitrate molten salt was performed. And then, the reaction experiment using each nitrate molten salt with approximately 2 mg of Na was performed. In this study, all DSC measurements were performed at 5 K/min as lower heating rate except kinetic consideration to obtain the precise phase change and reaction temperature within the detectable level for peak signal of DSC curves.

Table 1 Experimental condition

Pressure in reaction chamber	0.1 MPa
$NaNO_3$ / KNO_3 / $NaNO_3$-KNO_3 (sample)	50 mg
Na (sample)	2 mg
Al_2O_3 (reference)	100 mg
Heating rate	5 K/min
Test temperature	room temp.～673 K

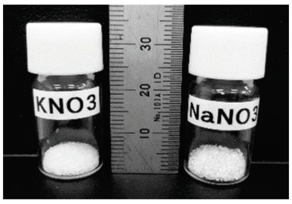

Fig. 1 Appearances of chemical reagent

III. Results and Discussion

1. Preliminary Experiment

The DSC curves for $NaNO_3$, KNO_3, $NaNO_3$-KNO_3 mixture based on the mass fraction of solar salt at the heating rate of 5 K/min are shown in **Fig. 2**. **Table 2** shows the comparison of the phase change temperature and enthalpy obtained from the DSC curve with literature data. For $NaNO_3$, it was confirmed that the endothermic peaks appeared at approximately 543 K and 580 K, corresponding to the phase transition ("tr." in Fig. 2) and the melting point ("m.p." in Fig. 2), respectively and these temperatures were comparable to the literature values. In addition, enthalpy can be obtained from the peak area of the DSC curve. The enthalpy for phase transition and melting point were 15 J/g and 178 J/g, respectively which were in good agreement with literature values. In the DSC measurement of KNO_3, the phase transition and melting point were also observed at approximately 403 K and 607 K, and these enthalpies were 48 J/g and 98 J/g respectively. These obtained values were consistent with previous findings. Since thermal behaviors of individual reagents were consistent with literature data, it was confirmed that the reliable DSC measurement was successfully done. Thus, for the next step, it is necessary to confirm that $NaNO_3$-KNO_3 mixture reproduces the solar salt feature. The DSC curve of $NaNO_3$-KNO_3 mixture shows the endothermic peaks at approximately 403 K and 502 K, respectively. The first peak at 403 K corresponded to the structural phase transition temperature of KNO_3 and the second peak at 502 K is lower than the melting points of both $NaNO_3$ and KNO_3, suggesting that they have eutectic melted and melting points were decreased. However, the present value of $NaNO_3$-KNO_3 eutectic melting is higher than the melting point of solar salt (491.4 K) reported in the previous study. In addition, the enthalpy was 167 J/g, which is larger than that of literature value (113 J/g). Therefore, it was considered that the composition of the solar salt could not be reproduced though the reagents of $NaNO_3$ and KNO_3 were prepared on the basis of the mass fraction of solar salt. In order to reproduce the solar salt, reheating (second heating) process was carried out because $NaNO_3$-KNO_3 mixture may not be homogeneous by first heating process. **Figure 3** shows the comparison of DSC curves for $NaNO_3$-KNO_3 mixture by first and second heating process at the heating rate of 5 K/min. The temperature and enthalpy for melting point obtained from DSC curve for $NaNO_3$-KNO_3 mixture by second heating was summarized in Table 2. It was apparently found that the melting point of second heating process became close to literature values.

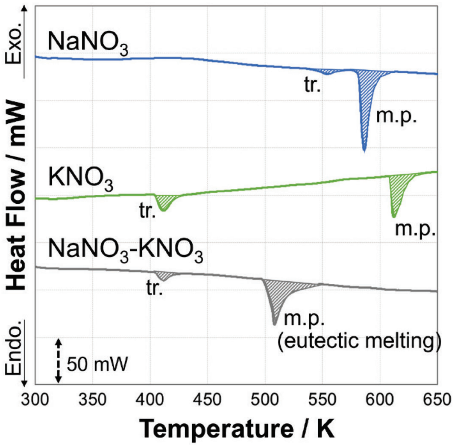

Fig. 2 DSC curves of $NaNO_3$, KNO_3 and $NaNO_3$-KNO_3

Table 2 Phase change temperature and enthalpy for molten salt

Reagent	Phase transition Temperature [K] Enthalpy [J/g]		Melting point Temperature [K] Enthalpy [J/g]	
	Present study	Literature	Present study	Literature
$NaNO_3$	543.0 15	550.0 6) 20.6 7)	579.8 178	583.0 6) 178 1), 174.13 8)
KNO_3	402.6 48	403.0 6) 46.35 7)	607.2 98	610.0 6) 100 9), 91.55 8)
$NaNO_3$-KNO_3	403.1 [a]/ - [b] 44 [a]/- [b]	403.0 6) 46.35 7)	501.8 [a]/ 493.9 [b] 167 [a]/ 116 [b]	491.5 8) 113 1,8)

a: first heating, b: second heating

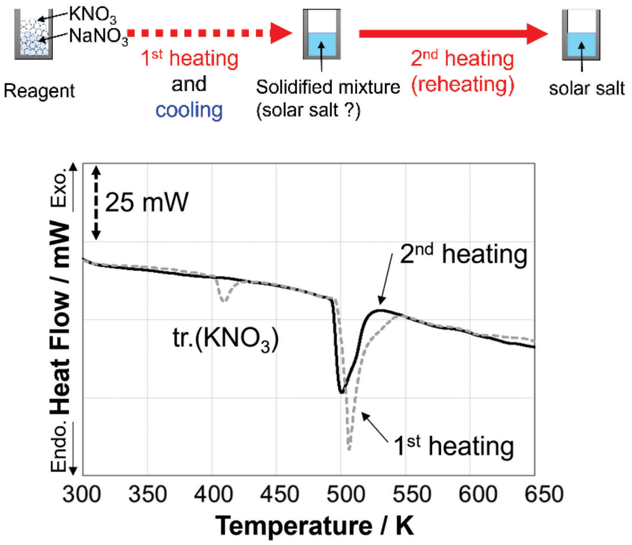

Fig. 3 DSC curves of $NaNO_3$-KNO_3

2. Reaction Experiment

As described in preliminary experiment, fundamental information of thermal behavior of each nitrate molten salt was obtained for the reactivity of nitrate molten salts with Na. Based on this information, DSC measurements for each nitrate molten salt with Na were performed.

The DSC curves for Na-NaNO3 and Na-KNO3 with each pure nitrate molten salt at the heating rate of 5 K/min are shown in **Figs. 4** and **5**. It was apparently confirmed that endothermic peak appeared at approximately 371 K in both DSC curves for Na-$NaNO_3$ and Na-KNO_3, which corresponds to the melting point of Na. In case of the DSC curve for Na-$NaNO_3$, the exothermic peak appeared around the melting point of $NaNO_3$ after the phase transition. This indicates the liquid phase reaction feature in liquid Na-liquid $NaNO_3$ contact. On the other hand, in case of the DSC curve for Na-KNO_3, the exothermic peak appeared at much lower than the melting point of KNO_3 (607 K) through the phase transition of KNO_3 (402 K) after Na melting. Though the overall reactions for Na-$NaNO_3$ and Na-KNO_3 have been proposed as Eqs. (1) and (2) in previous studies, further investigation and analysis of the reaction products may be necessary to determine the reaction mechanism.[4)]

$$10Na + 2NaNO_3 \rightarrow 6Na_2O + N_2 \tag{1}$$

$$10Na + 2KNO_3 \rightarrow 5Na_2O + K_2O + N_2 \tag{2}$$

Figure 6 shows the DSC curves for Na-$NaNO_3$, Na-KNO_3 and Na-$NaNO_3$-KNO_3 at the heating rate of 5 K/min. The phase transition of KNO_3 and the eutectic melting of $NaNO_3$-KNO_3 at around 500 K were observed from the DSC curve for Na-$NaNO_3$-KNO_3. Besides, the sharp exothermic peak with thermal runaway feature was observed just after the eutectic melting of $NaNO_3$-KNO_3. This reaction behavior was consistent with the DSC measurement results in the previous study.[4)] Moreover, in comparison with Na-$NaNO_3$ and Na-KNO_3 reaction, this reaction occurs at same temperature range of Na-KNO_3 reaction. However, the thermal runway feature was observed in case of the first heating of Na with the reagents of $NaNO_3$ and KNO_3 granule as starting materials. As described in the preliminary experiment, solar salt could not be reproduced by first heating process of $NaNO_3$-KNO_3 mixture. Thus, the DSC curve for Na-$NaNO_3$-KNO_3 does not indicate thermal behavior of Na-solar salt as reported in the previous study.[4)] In order to simulate the Na-solar salt reaction, the DSC measurement for second heated $NaNO_3$-KNO_3 shown in Fig. 3 with Na should be carried out.

Figure 7 shows a comparison of DSC curves for Na-solar salt and Na-$NaNO_3$-KNO_3 at the heating rate of 5 K/min. As described in Fig. 6, the reaction behavior of Na-$NaNO_3$-KNO_3 by first heating process indicated thermal runaway feature (dashed line). However, in case of second heated $NaNO_3$-KNO_3 (solar salt) with fresh Na, the broad exothermic peak appeared after the solar salt melting (solid line). This indicates that reaction rate is slower than that of first heating process with thermal runaway feature.

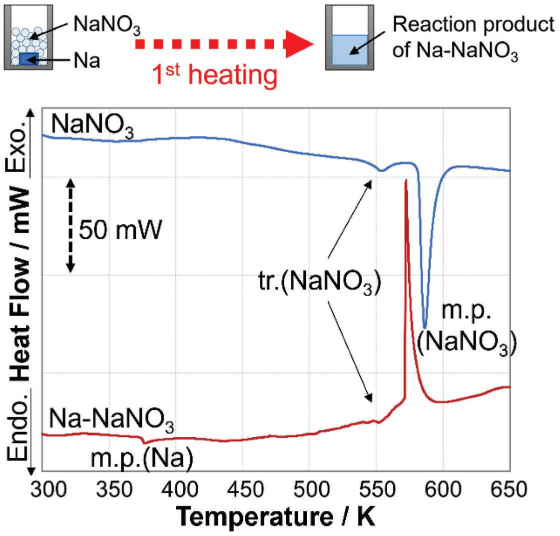

Fig. 4 DSC curves for Na-$NaNO_3$ and $NaNO_3$

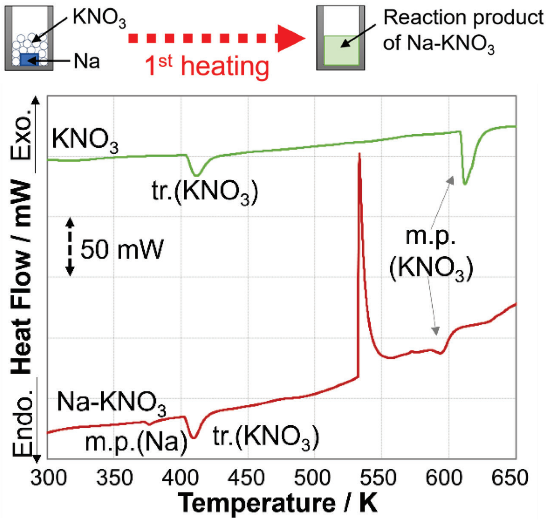

Fig. 5 DSC curves for Na-KNO_3 and KNO_3

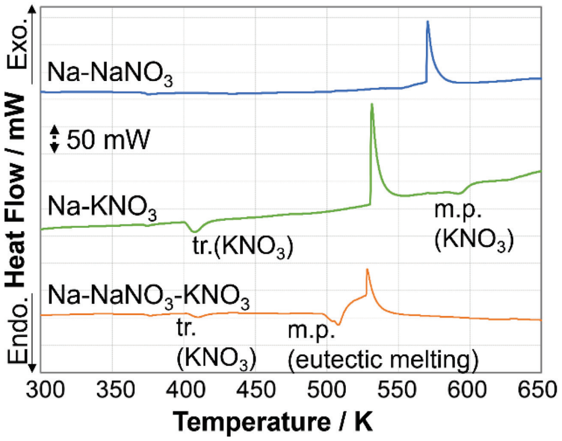

Fig. 6 DSC curves for Na-NaNO$_3$, Na-KNO$_3$ and Na-NaNO$_3$-KNO$_3$

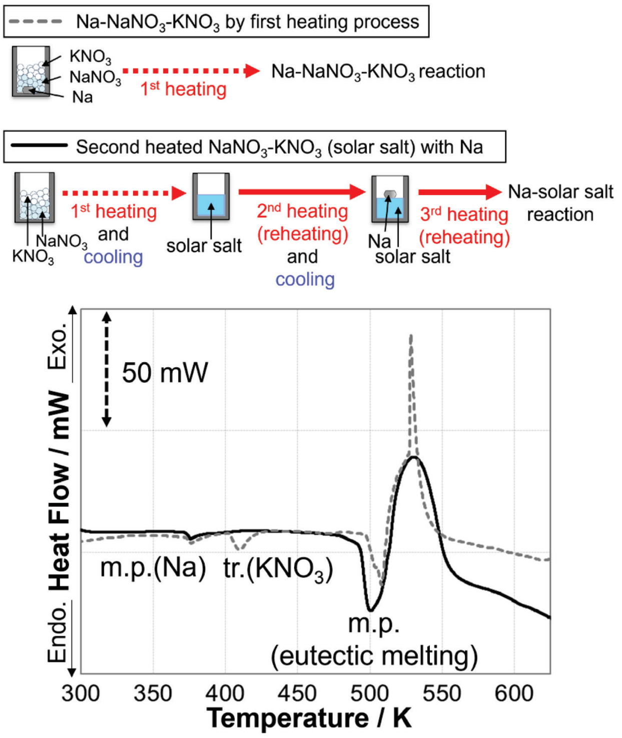

Fig. 7 DSC curves for Na-solar salt and Na-NaNO$_3$-KNO$_3$

3. Kinetic Consideration

In light of the reaction behavior of Na-solar salt as described in Fig. 7, DSC measurements were performed at different heating rates to confirm the possibility of kinetic evaluation. **Figure 8** shows typical DSC curves for Na-solar salt at the heating rates of 2, 5, 7.5 and 10 K/min. The exothermic peaks shift systematically to higher temperatures with increasing heating rate from 518 K to 548 K, which is possible to evaluate the kinetic parameters. Therefore, the DSC measurements were conducted four times in each heating rate to secure repeatability and to consider the uncertainty. Based on the peak top temperature of DSC curves, kinetic parameters for rate constant were evaluated by Kissinger method.[10] In this method, from the relationship between the heating rate β and the peak top temperature T_p, the kinetic parameters can be obtained from the slope and intercept of the plot called "Kissinger plot" which is plotted $\ln(\beta / T_p^2)$ against $1 / T_p$.

Figure 9 shows the Kissinger plot of Na-solar salt reaction with the temperature range of 298-650 K at the heating rates of 2, 5, 7.5 and 10 K/min. We used the least squares method for approximation of these plots. From regression line of Kissinger plots, the activation energy E_a and the Arrhenius' pre-exponential factor (frequency factor) A were calculated, and these parameters were compared with our reported value for sodium-water reaction which takes place if a heat transfer tube in the steam generator is failed in a sodium-cooled fast reactor (**Table 3**).[11] Sodium-water reaction pathways are two steps, the primary reaction (Na-H_2O) in which NaOH is generated and the secondary reaction (Na-NaOH) in which Na_2O is generated with H_2 as shown in Eqs. (3) and (4).

$$Na + H_2O \rightarrow NaOH + 1/2H_2 \qquad (3)$$

$$Na + NaOH \rightarrow Na_2O + 1/2H_2 \qquad (4)$$

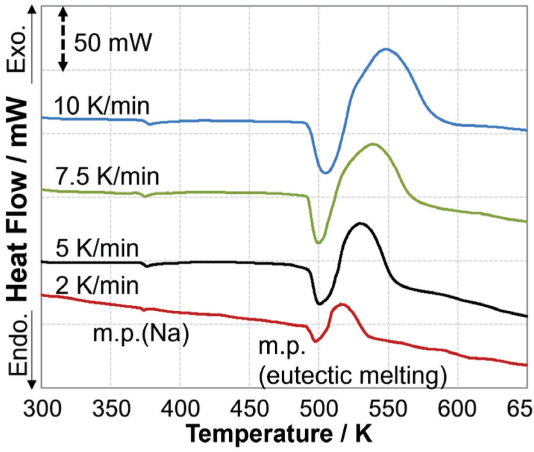

Fig. 8 DSC curves for Na-solar salt at the heating rate of 2 K/min, 5 K/min, 7.5 K/min, 10 K/min

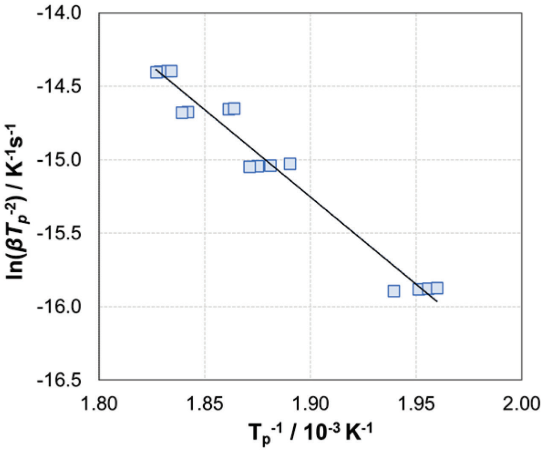

Fig. 9 Kissinger plot of Na-solar salt

However, it is difficult to perform kinetic analysis of the primary reaction for sodium water reaction by thermal analysis because of the extremely rapid reaction rate. In other words, Na-H_2O reaction is much faster than Na-solar salt reaction.

Compared with the secondary reaction for sodium water reaction, the activation energy and pre-exponential factor for Na-solar salt reaction are smaller than those of Na-NaOH reaction. This indicates that the reaction rate for Na-solar salt at 510-547 K as obtained reaction onset, is faster than that of Na-NaOH reaction at 653-675 K. But, for practical accidental event, initial sodium temperature is around 773 K. Therefore, higher temperature region should be assumed for the failure of heat transfer tube of sodium-molten salt heat exchanger.

Figure 10 shows a comparison of the rate constant of Na-solar salt reaction with Na-NaOH reaction. The solid line is reaction onset temperature range obtained in the present and previous studies and dashed line is extrapolated region estimated using kinetic parameters as shown in Table 3. The rate constant of Na-solar salt at lower temperatures or around reaction onset is much larger than that of Na-NaOH reaction. Besides, the rate constant of Na-solar salt reaction at higher temperature (around 773 K) was still remaining large in comparison with that of Na-NaOH reaction. Thus, it could be assumed that Na-solar salt reaction occurs in the time frame of the accident such as the failure of heat transfer tube of sodium-molten salt heat exchanger.

Table 3 Kinetic parameters

parameters	E_a / kJ/mol	ln (A / s^{-1})
Na-solar salt	98.6 ± 15	16.7 ± 11
Na-H_2O (primary)	Extremely rapid	
Na-NaOH (secondary) [11]	161	23

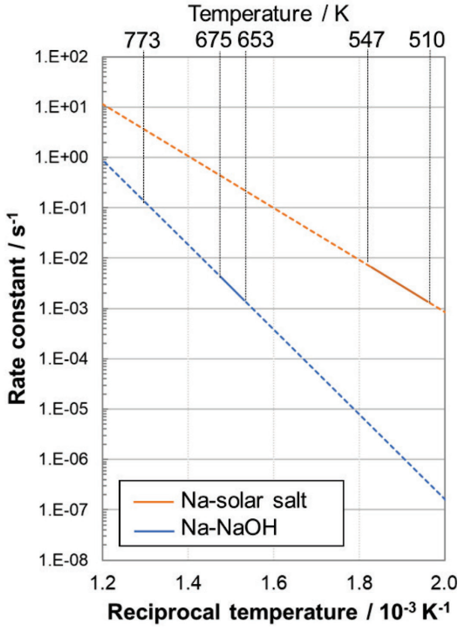

Fig. 10 Rate constant for Na-solar salt and Na-NaOH

IV. Conclusion

In this study, to clarify reaction behavior of Na-nitrate molten salt caused by the heat transfer tube failure, the DSC measurements of the reaction between Na and nitrate molten salts were performed. Based on the DSC measurements, it was found that Na-solar salt reaction occurred after the solar salt melting induced by eutectic melting of $NaNO_3$-KNO_3, which is the same temperature range of Na-KNO_3 reaction. Besides, it was confirmed that the sharp exothermic peak with thermal runaway feature appeared in case of first heating of Na-$NaNO_3$-KNO_3 mixture on the basis of mass fraction of solar salt as reported in the previous study. Moreover, the broad exothermic peak for Na-solar salt was successfully obtained in case of second heated $NaNO_3$-KNO_3 mixture with Na.

Based on the peak top temperature of DSC curves for Na-solar salt, kinetic parameters for rate constant were estimated by Kissinger method and compared with those of sodium-water reaction due to the failure of heat transfer tube in the steam generator. It was revealed that the rate constant of Na-solar salt reaction at actual accidental temperature was larger than that of Na-NaOH reaction as secondary reaction for sodium-water reaction. Therefore, it could be assumed that Na-solar salt reaction occurs in the time frame of the accident such as the failure of heat transfer tube of sodium-molten salt heat exchanger. It is expected that these results can be reflected in the safety assessment of the SFR with TES system with sodium-molten salt heat exchanger.

For the next step, in order to finally determine the reaction mechanism of Na-solar salt reaction, further investigation of solid products after DSC measurements by using X-ray diffraction analysis is required.

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