The Suppression Effect of Ti Nanoparticle Concentration on Sodium-Water Reaction

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1. Introduction

Liquid sodium (Na) has been used as a reactor coolant in Sodium-cooled Fast Reactor (SFR) which is one of the Generation IV nuclear reactors, but this strategy is risky because when liquid Na contacts water, Sodium-Water Reaction (SWR) occurs. The reaction phenomena of Na with water contact has been studied to evaluate the access of using Na coolant in nuclear power plant [1-5].

In a design of sodium-cooled fast reactor, thermal energy is transported from high-temperature liquid Na to low-temperature water through a heat exchanger [6, 7]. If any leakage or rupture occurs during the operation of this heat transfer system, highly pressurized liquid water can penetrate into the liquid Na channels; this contact should instantly cause SWR (Fig. 1). As reaction continues, liquid water is soon vaporized by pressure drop and huge amount of reaction heat. This generated water vapor expands large reaction area and increases sodium-water vapor reaction process. Therefore, the rapid generation of reaction product (like H_2) and water vapor increases the system pressure that can cause the system failure in SFR.
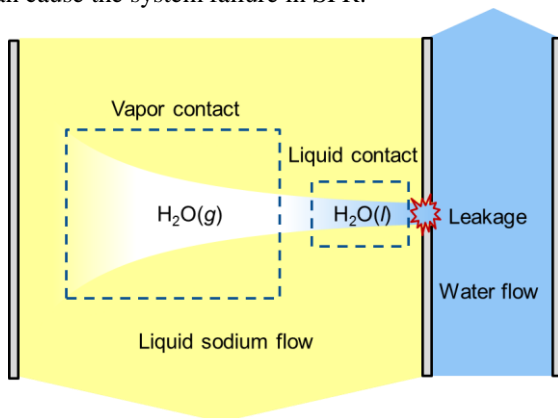

Fig. 1. Schematic of SWR in a heat exchanger.

To reduce this strong chemical reaction phenomena between Na and water, an idea suggested to disperse nanoparticles (NPs) in liquid Na [8]. The experimental results showed the reduction of hydrogen generation rate and reaction heat. Recently we have suggested Na-based Titanium nanofluid (NaTiNF) which containing Ti NPs (<100nm) in liquid Na [9]. We experimentally demonstrated the suppressed reactivity of NaTiNF when

it contacts with water and water vapor [9-11]. The role of dispersed Ti NPs in liquid Na to suppress SWR was considered by chemical interaction. Theoretical approach to the chemical interaction between Na atoms and Ti NPs has been investigated by ab-initio calculation [12]. The other role of Ti NPs was interruption the contact between Na and water molecules at the interface [11]. The conjecture said the suppressed reactivity of Na could be controlled by the concentration of Ti NPs on the Na surface where Na contacts with water molecules first.

For controlling the suppression effect of Ti NPs in SWR, we have focused on evaluating the role of Ti NPs at the Na-water interface. In this research, we have dispersed 100nm of Ti NPs in liquid Na from 0.1 vol. % to 0.7 %. To evaluate the suppression effect in SWR, the reactor is design that liquid Na at 104 °C reacts with 2.5ml of distilled water [10]. The reaction rate of SWR is followed by parabolic reaction law.

2. Experimental arrangement

2.1 Experimental set-up

To compare reaction phenomena of NaTiNF-water reaction with different Ti NP concentration, the experimental set-up is the as previous study [9, 10]. The reactor is designed liquid Na directly reacts with liquid water. It is consisted of the crucible sodium container, water storage, pressure sensor line, vacuum pump line and thermocouple (Fig. 2). The reactor is heated by a conduction heater that consisted of the cartridge heater. Temperature of the reactor is monitored by k-type thermocouple. The reactants (Na or NaTiNF) are prepared under the Argon gas condition. They are stored in the crucible which is perfectly sealed. When the reactor temperature reaches reaction temperature (T_R = 104), the reactor is detached from the heater and evacuated by the vacuum pump. To trigger SWR, a valve between the reactor and a water storage tank open to inject water into the reactor. Absolute pressure transducer monitors the pressure change during the reaction. In this experiments, approximately 0.2g of Na or NaTiNF reacts with 2.5ml of distilled water.
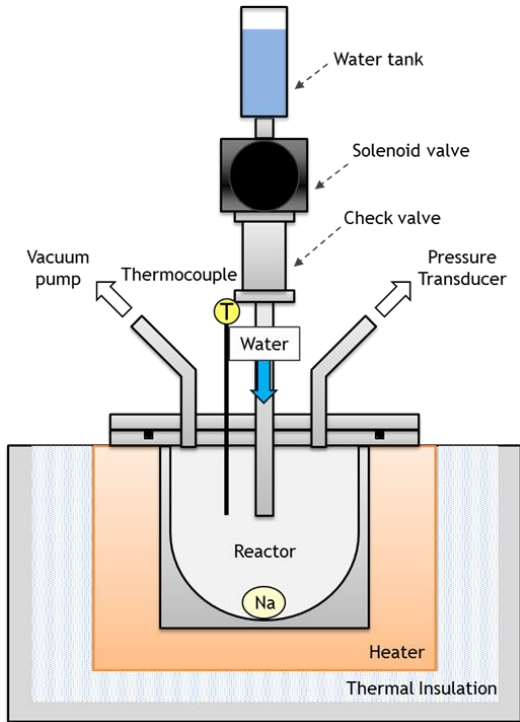
Fig. 2. The reactor is designed to inject a distilled water to liquid Na to trigger an SWR.

2.2 Hydrogen generation during SWR

During the SWR, H_2 generation increases the inner pressure of the reactor. To compare reaction phenomena, reaction rate of SWR should be obtained. However, the difference of the reaction rate between Na and NaTiNF cannot be easily obtained from pressure increase. SWR always includes a temperature increase inside the reactor because the chemical reaction is exothermic. Reaction heat released by SWR causes H_2 volume expansion which raises the inner pressure with constant reactor volume. Therefore, measured pressure should be converted to moles of H_2 (N_{H2}) by applying the ideal gas law assuming isentropic process for eliminating pressure increase by reaction heat.

$$P_2 = P_1 \, (T_2/T_1)^{\lambda/\lambda-1}$$

P_1, T_1 are measured pressure and temperature, T_2 is ambient temperature (= 30 ℃), λ is specific heat ratio. Since the volume of the reactor is fixed, the pressure change of SWR can be converted to an expected volume change by assuming an isothermal process at atmosphere pressure.

$$V_2 = V_i \, (P_2/P_{atm})$$

V_i and P_{atm} are reactor volume and atmosphere pressure. The number of moles of H_2 regarding to reaction time can be calculated from volume of H_2 by Avogadro's law at STP. *Vm* is 22413. 774 ml/mol.

$$N_{H2} \, [mol] = V_2/V_m$$

The final number of moles of H_2 generated (N_{final}) at reaction completion is obtained when the reactor is cooled down to 30 ℃, 5 min after the beginning of SWR. When $N_{H2}/N_{final} = 1$, the reaction was consider to be complete (Fig. 3).
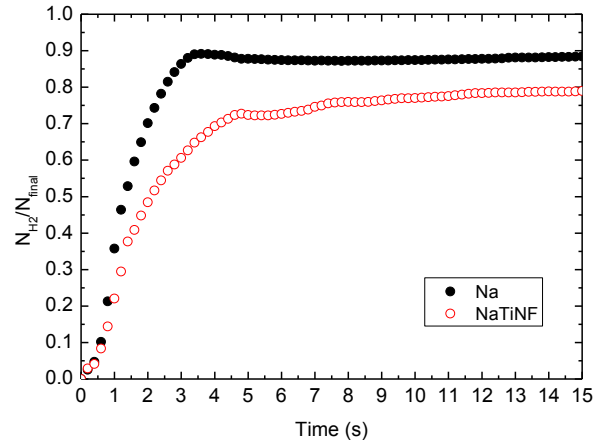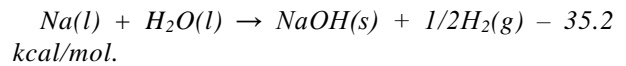

Fig. 3. Hydrogen generation of Na vs NaTiNF at 104 ℃.

To determine the reaction rate, a parabolic law was used to determine the reaction rate of NaTiNF with water. This reaction is assumed to follow only the most common chemical equation of SWR [3]:

$$Na(l) \; + \; H_2O(l) \; \rightarrow \; NaOH(s) \; + \; 1/2H_2(g) \; - \; 35.2 \; kcal/mol.$$

N_{H2} generated during SWR to time t is simply the half the number of moles of NaOH that have been produced during Na-water reaction up to that time; N_{H2} is defined as the increase in the quantity of reaction products during the rate-determining step [13]:

$$(N_{H2}/ \, N_{final})^2 = k_1 t$$

All reaction rates in the Na or NaTiNF-water reaction have been determined by the initial rate of H_2 generation. The rate constant k_1 determines the kinetics of the NaTiNF-water reaction.

3. Results and discussion

3.1 Ti NPs concentration

Ti NPs are dispersed in liquid Na with Ti NP fraction at 0.1, 0.2, 0.4 and 0.7 % (Fig. 4). The actual Ti concentration in liquid NaTiNF is not easily defined. Therefore, NaTiNF specimens were dissolved in ethanol and the solution was analyzed using Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). A sample of 0.2 g of NaTiNF contains Ti concentration, c_{Ti}, from 0.1873 to 0.2728 mol/L (Table.

1). The measured Ti concentration in NaTiNF specimens through ICP-AES analysis represents the total amount of Ti in the specimen. Which is Ti bulk concentration in NaTiNF specimen.
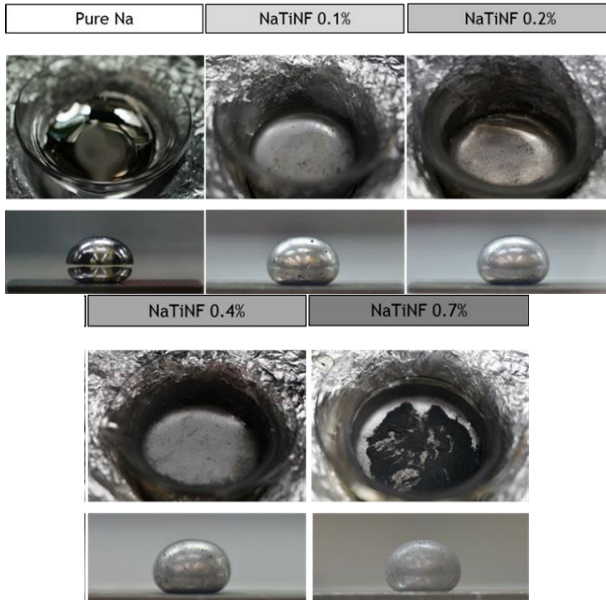

Fig. 4 Dispersion of Ti NPs in liquid Na with Ti fraction variation + droplet view.

Table 1. The details of specimens.

Specimens	m_{NaTiNF} (g)	V_{NaTiNF}(ml)	c_{Ti} (mol/L)
0.1%	0.1988	0.2038	0.1873
0.2%	0.2064	0.2114	0.2195
0.4%	0.2031	0.2071	0.3264
07%	0.2078	0.2124	0.2728

3.2 Reaction rate of NaTiNF

For the NaTiNF-water reaction with Ti fraction variation, procedure is the same as in previous trials [10]. The amount of reactant was ~0.2 g of Na and 2.5 mL of distilled water. The amount of distilled water was sufficient to react with Na completely. Reaction temperature, T_R, was ~104 ℃, so Na was maintained as liquid. All the reaction experiments are conducted at least 3 times for each cases.

To clearly compare the reaction behavior in NaTiNF-water reaction with Ti faction variation, the reaction rate is was obtained by the parabolic law as previously [10]. The proportion of H_2 generated increased with reaction time during NaTiNF-water reaction. The slope of graph represents the reactivity of specimen (Fig. 5). Reaction rate is determined at the initial reaction stage because Ti NPs strongly influence the initial stage of the reaction. As the dispersed Ti NPs fraction increases, reaction

becomes slow. However, the slop of NaTiNF-0.4 % is lower than NaTiNF-0.7% because contained Ti concentration in NaTiNF-0.4 % case is lower than 0.7 % case.
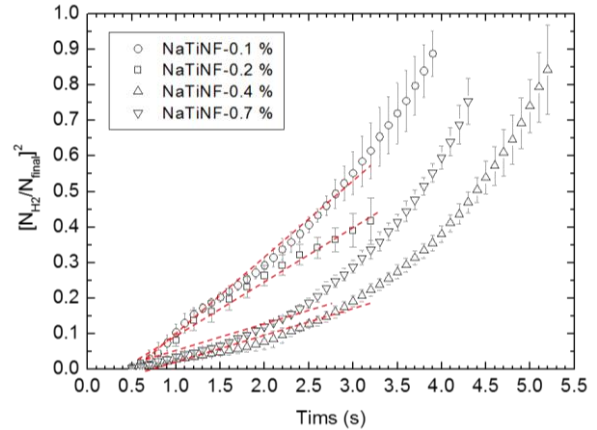

Fig. 5. NaTiNF-water reaction with Ti NP fraction at T_R = 104 ℃.

Table 2. Rate constants of specimens

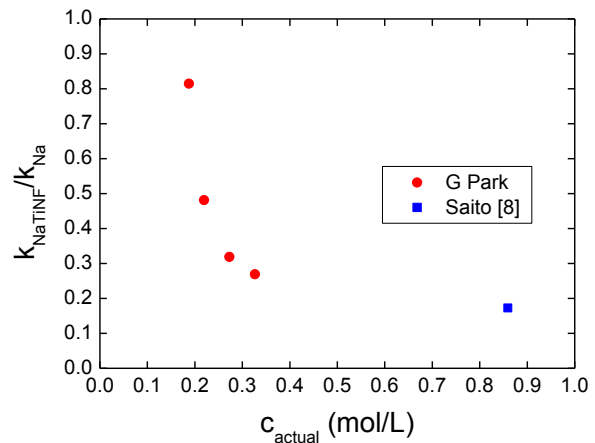| Specimens	c_{Ti} (mol/L)	k_1 (s^{-1})	k_{NaTiNF}/k_{Na}
Na	0	0.3176	1
NaTiNF	0.18739503	0.2614	0.8148
	0.21954984	0.1549	0.4812
	0.27280306	0.1023	0.3189
	0.32647503	0.0862	0.2687

Fig. 6 The reactivity ratio of NaTiNF vs Ti concentration.

The rate constant of NaTiNF will be compared with the That of Na as previously [10]. The ratio of suppressed reaction rate of NaTiNF regarding to reaction rate of Na, the reactivity ratio k_{NaTiNF}/k_{Na} is varied from 0.8148 to 0.2687 (Table 2). The rate constants (Fig. 6) decreased as Ti fraction increased to 0.4% and seems to have saturated at that fraction,

although the constant was slightly higher at 0.7% than at 0.4 %. This result indicates that suppression of SWR reactivity by NaTiNF is influenced by the dispersed Ti concentration.

Additionally, the Ti bulk concentration of Saito's work was calculated based on the Ti 2 atomic % assuming Ti NPs were uniformly dispersed in liquid Na, since he did not present the exact Ti concentration in the specimen [8]. However, the dispersion of Ti NPs in liquid Na was not exactly matched with initial Ti vol. %. Therefore, the actual Ti bulk concentration of Saito's work could be differ from the calculated value in this work.

3.3 Discussion about the role of Ti NPs on surface reaction

SWR initially occurs at the interface of Na and water where water molecule initially contact with Na atoms. Which is called surface reaction. From the reaction behavior of NaTiNF, the suppressed effect is clearly shown at the beginning of the reaction (Fig. 5). Therefore, to investigate the suppression effect of Ti NPs in SWR, the role of Ti NPs in surface reaction is important. When Ti NPs are dispersed in liquid Na, some will be maintained in the bulk state and some should be assembled at the surface of Na [14]. At the Na surface, two regions are expected. One is bared surface that no Ti NPs are existed and the other is Ti NPs interacted surface that Ti NPs assembled region (Fig. 7).
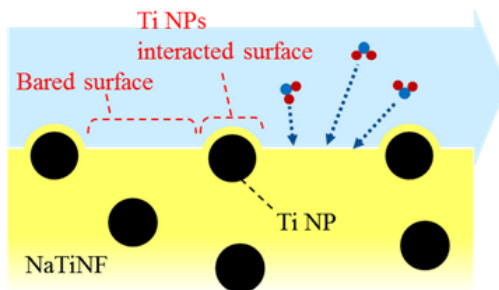

Fig. 7 Reaction surface of NaTiNF.

When water molecules come close to the surface of Na, they should be favor to react with Na atom at bared surface. In the other word, Ti NPs at the Na surface interrupt the contact between Na and water. Therefore, how many Ti NPs are settled on Na surface could control the reactivity of SWR. This conjecture is consistent with suppression effect of NaTiNF with Ti fraction variation. Higher Ti concentration in NaTiNF should contain higher Ti NPs on Na surface. However, the exact number of Ti NPs on the Na surface is still unknown, since it is hard to observe the assembly of Ti NPs on liquid surface.

4. Conclusions

The suppressed reactivity of NaTiNF-water reaction is investigated with variation of dispersed Ti concentration. Ti NPs are dispersed in liquid Na with different volume fraction. The actual Ti concentration in NaTiNF is measured by ICP-AES device. From the result, the reactivity of SWR is decreased with Ti concentration. However, as Ti concentration higher, reactivity of NaTiNF becomes saturated. The suppression result indicates that the suppression effect of SWR is strongly affected by Ti concentration. The dispersed NP concentration becomes a key factor to control the reactivity of SWR.

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