SUPPRESSION OF CHEMICAL REACTIVITY OF SODIUM-TITANIUM NANO FLUID IN SODIUM-WATER VAPOR REACTION

Gunyeop Park, Soo Jae Kim, and Je Hyun Baek
Department of Mechanical Engineering
Pohang University of Science and Technology (POSTECH)
Address
gpark@postech.ac.kr; akilleus@postech.ac.kr; jhbaek@postech.ac.kr

Hyun Soo Kim, Sun Ryung Oh, Hyun Sun Park* and Moo Hwan Kim
Department of Nuclear Engineering Division of Advanced Nuclear Engineering
Pohang University of Science and Technology (POSTECH)
Corresponding Address
hejsunny@postech.ac.kr

ABSTRACT

For the suppression of the high chemical reactivity of liquid sodium with water, the suspension of nanoparticles in liquid sodium has been suggested in 2010 [1]. This mitigation measure based on the finding of nanoparticles that play a role as a reaction inhibitor to reduce the chemical reaction rate between a liquid sodium and water. Therefore we have investigated the suppression effect on the Sodium-water Vapor Reaction (SVR) using the method of Titanium (Ti) nanoparticles (NPs) suspension. Sodium-Titanium Nano Fluid (NaTiNF), i.e., liquid sodium with dispersed Ti NPs ($\leq$ 100 nm) at 0.2 Vol. %, is prepared. In the test, the solid sodium is heated above the melting temperature of sodium, and the water vapor passes over the surface of liquid sodium under the atmosphere pressure. High-speed camera (500 frame/s) was used to visualize the surface reaction process. The increase of temperature due to exothermic chemical reaction in NaTiNF-water vapor reaction is also measured with recording the surface reaction phenomena. The NaTiNF-water vapor reaction demonstrates the lower temperature increment (12.78 ±1.09 ˚C/s) than that of Na case (17.45 ±0.93 ˚C/s). The suppressed reactivity of NaTiNF is 63% of Na-water vapor reaction. This results suggest that the chemical reactivity of liquid sodium with water reaction can be suppressed by the present of NPs in liquid sodium.

KEYWORDS
Sodium-cooled fast reactor, liquid sodium, nanoparticles, chemical reactivity, sodium-water vapor reaction

1. INTRODUCTION

Liquid metal has been considered as a high performance heat transfer material in many heat removal systems. Especially, liquid sodium has been used as a reactor coolant in Sodium-cooled Fast Reactor (SFR) which is one of the Generation IV nuclear reactors. Even though the use of liquid sodium in energy conversion system brings both high performance and efficiency, liquid sodium still has a potential risk because of its high chemical reactivity. When liquid sodium comes in contact with oxygen or water moisture, it rapidly reacts with them and releases enormous heat and reaction products. According to the well-known chemical reaction paths of sodium-water reaction, hydrogen and sodium hydroxide are generated with reaction heat as equation (1, 2) in Table 1, although the exact reaction path is not well developed [2].

Table I. Chemical equations of SWR

Chemical equations	ΔH (kcal/mol)	
$Na(l) + H_2O(l) \rightarrow NaOH(s) + \frac{1}{2}H_2(g)$	-35.2	(1)
$Na(l) + H_2O(g) \rightarrow NaOH(s) + \frac{1}{2}H_2(g)$	-45	(2)
$2Na + H_2O \rightarrow NaOH + NaH$	-47.37	(3)
$Na(l) + \frac{1}{2}H_2(g) \rightarrow NaH(s)$	-13.7	(4)
$Na(l) + NaOH(s) \rightarrow Na_2O(s) + \frac{1}{2}H_2(g)$	+2.6	(5)
$Na(l) + NaOH(s) \rightarrow Na_2O(s) + \frac{1}{2}H_2(g)$	-31.08	(6)
$2Na(l) + NaOH \rightarrow Na_2O + NaH$	-11.1	(7)

In a sodium-cooled fast reactor (KALIMER-600) designed by Korea Atomic Energy Research Institute, liquid sodium (526 ˚C at 0.1 MPa) indirectly exchanges heat with low temperature water (230 ˚C at 19.5 MPa) through shell-and-tube type heat exchanger in a steam generator that is connected to a power generation system [3]. If any of small leakage or rupture occurs during the operation of liquid sodium-water heat exchanger, high pressurized steam will penetrate into liquid sodium coolant instantly. This causes an explosive Sodium-Water Reaction (SWR) that generates high reaction heat and enormous hydrogen gas which threats the safety operation of the nuclear power plant. Therefore, SWR still remains as a high risk in operating SFR.

Alternative methods to guarantee the safe use of liquid sodium have been suggested such as using double-layer tubes instead of single layer tube in a heat exchanger, or changing the liquid metal coolant to a lead bismuth [4]. Another option is to use a chemical method to reduce SWR risk by using an aqueous solution of Epsom salt ($MgSO_4$+7H2O) instead of pure water [5]. When a solid sodium is dropped into the Epsom salt solution, a sodium dissolution without any flame occurs at a certain solute concentration; this results in sodium being dissolved slowly in NaOH solution.

Few researchers have focused on suppressing the chemical reactivity of liquid sodium using nano technology. Jun-ichi Saito suggested suspended titanium nanoparticles (10nm) in liquid sodium forming sodium-nanoparticles cluster that makes the strong atomic bond between sodium atoms and nanoparticles [1]. The authors compared released heat of sodium-water vapor reaction. The temperature increase in the reaction of titanium suspended liquid sodium is lower than liquid sodium. The reaction rate of sodium with suspended nanoparticles is also lower than liquid sodium according to SWR. G Park demonstrated the suppressed chemical reactivity of sodium-based Titanium nanofluid (NaTiNF) through liquid sodium-water reaction experiment [6]. The authors dispersed titanium nanoparticles (<100nm) at 0.214 vol. % in liquid sodium and performed sodium (0.2g) – water (2.5ml) reaction measuring hydrogen generation rate. The study indicated that the Ti NPs are well distributed on the surface of liquid sodium and showed suppressed reaction behavior of NaTiNF as Jun-ichi Saito's work. Moreover, this study conjectured that these Ti NPs on the surface of liquid sodium interrupt the contact of water molecules with sodium atom during the surface reaction, acting to suppress the reaction rate at the beginning of the reaction.

The present study focuses on the effect of Ti NPs in the surface reaction between sodium and water vapor interaction. From the previous work [1], it is suspected that how the reaction behavior of SWR change by bigger size of NPs. Therefore Ti NPs (<100nm) are employed as an inhibitor to suppress the surface reaction of sodium with water. In contrast to the previous work which performed instant reaction of sodium with excess of liquid water [6], relatively slow reaction is perform. The suppressed reaction rate of NaTiNF with water vapor is experimentally demonstrated and visualization is performed using high-speed camera. The behavior of surface reaction between Na and NaTiNF has been compared from the begging of reaction.

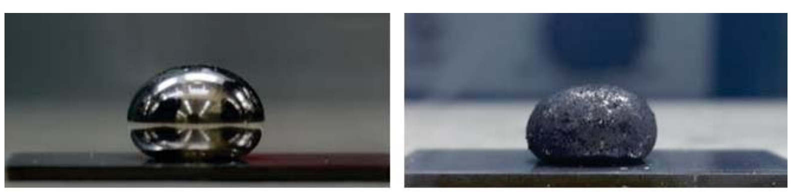
2. EXPERIMENTS AND RESULTS

2.1. Preparation of NaTiNF

Sodium-Titanium Nano Fluid (NaTiNF) is prepared as titanium nanoparticles ($\leq$ 100nm) are dispersed in liquid sodium at 180˚C with volume fraction of 0.2% [6]. The NPs volume faction has been selected the same as the previous researches [1, 6] because of the consistence of reaction investigation. Liquid Na has shiny silver color with reflective characteristic (Fig. 1 a) while NaTiNF appears to be less shiny and rather dull black color (Fig. 1 b). The characteristics of NaTiNF, such as an interaction between nanoparticle and Na, and thermal conductivity are explained in the previous works [6, 7]. For the Sodium-water Vapor Reaction (SVR), 0.2g of Na and NaTiNF spherical droplets are prepared (Fig. 2) and inserted in the reactor.

(a) (b)

Figure 1. (a) Liquid Na, (b) NaTiNF.



(a) (b)

Figure 2. (a) Na, (b) NaTiNF.

Prepared Na and NaTiNF are individually settled on the reactor under the inner condition in a glove box for maintaining non-oxide condition (Fig. 3).

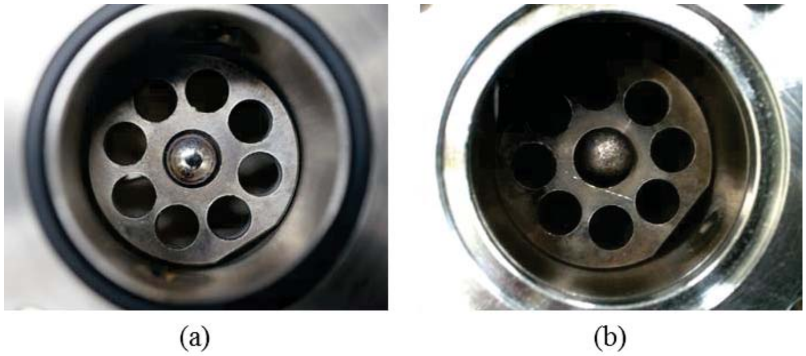


Figure 3. (a) Na, (b) NaTiNF.

2.2. Experimental set-up

Experimental facility is mainly consisted of two parts: steam generator and reactor (Fig. 4). A steam generator (2000ml, 600W) is filled with distilled water. Inner temperature of the steam generator is being monitored by two k-type thermocouples that installed at the upper and bottom of the generator. Distilled water inside the steam generator is boiled by thermal conduction heating controlled by a voltage controller. Water vapor is transported through a transport line (1/4” flexible stainless steel tube) from the steam generator to the reactor. The transport line is finely covered by ribbon heater (100W) controlled by voltage controller in order to maintain the temperature of water vapor above 100˚C. During the passing of water vapor through the transport line, water vapor temperature is monitored by k-type thermocouple inserted into an inside of the line. In order to maintain stable water vapor before supplying into the reactor, water vapor is drained until reaching 100˚C for 5min. The reactor is settled on a conduction heater. The heater is made of copper block in which four cartridge heaters are inserted in. The heater is covered by ceramic insulation and aluminum jig. The reactor is heated by PID controller to reach the target temperature in few tens of minutes. High-speed camera (~500 frame/s) is installed above the reactor recording reaction phenomena during reaction.

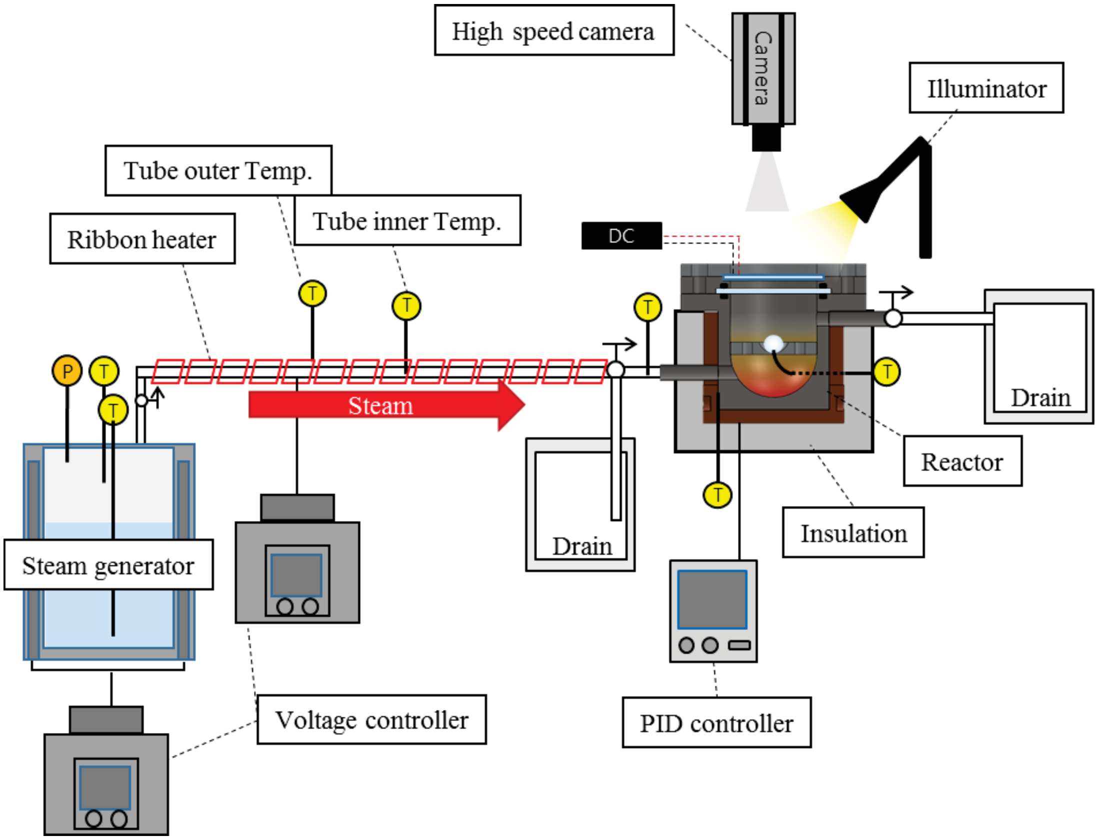


Figure 4. Schematic of experimental set-up.

When the reactor is heated up to the target temperature (105 °C in this experiment), water vapor is injected into the reactor through the line at the bottom of reactor (Fig. 5). Injected water vapor passes through the holes in an intermediate plate and reacts with sodium. Reaction products, mostly hydrogen gas and un-reacted water vapor are vented through upper vent line to the environment.

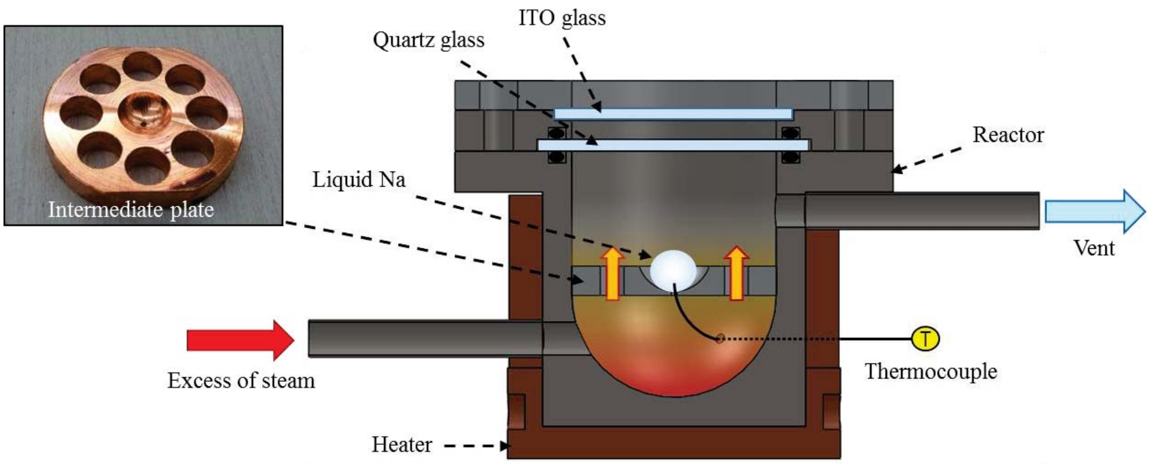


Figure 5. Schematic of the reactor.

Temperature of Na is directly measured by k-type thermocouple that is inserted from the bottom of the intermediate plate to sodium. Reaction temperature is above the melting point of Na. In order to visualize the surface reaction phenomena, the reactor is sealed with quartz glass by O-ring. To ensure a clear visualization, a possible water vapor condensation on quartz glass has to be prevented. Therefore, ITO electric heating glass is installed just above the quartz glass to indirectly heat up the quartz glass.

2.3. Results

Temperature of Na and NaTiNF has been monitored since SWR is exothermal chemical reaction [8]. K-type thermocouple has Temperature data is collected at every 0.2sec by data acquisition system (Agilent 34970A). The k-type thermocouple has a specific error of 1.1 °C. However this error has been ignored because of the difference in temperature increment between Na and NaTiNF is larger than the thermocouple error. The reaction of Na and NaTiNF cases have been repeated 3 times for a reproducibility. Reaction begins at 5s resulting an increase in temperature (Fig. 6). The temperature increment of NaTiNF is obvious different from that of Na from the initial reaction period (from 5s in Fig. 6). The temperature increment of Na shows curve like increase until it reaches to the maximum point. However, that of NaTiNF case shows two different increment rate until it reaches to the maximum point. At the initial reaction period, temperature increment rate of Na (Fig 6 a) is higher than that of NaTiNF (Fig. 6 b-1).

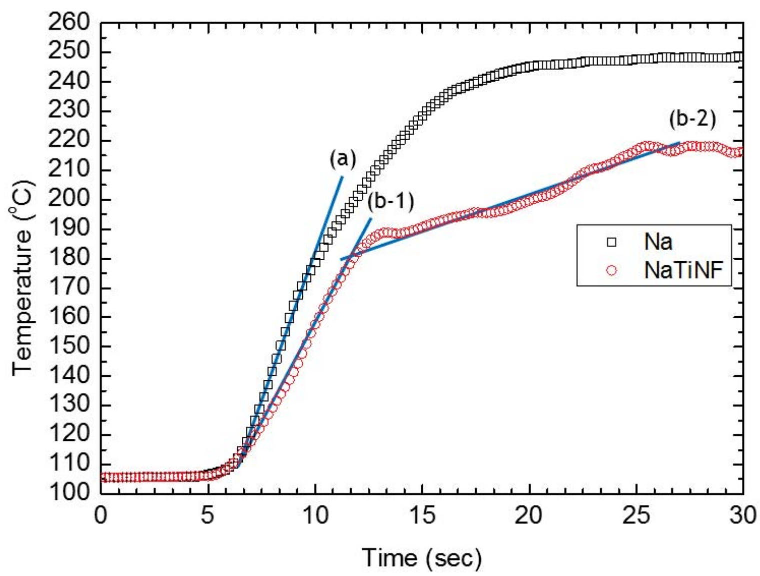
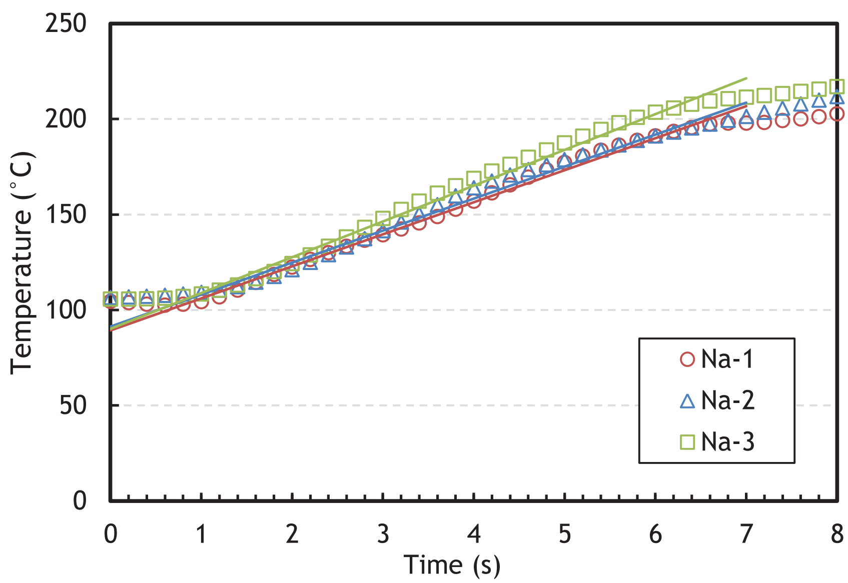


Figure 6. Temperature increment of Na and NaTiNF with time variation

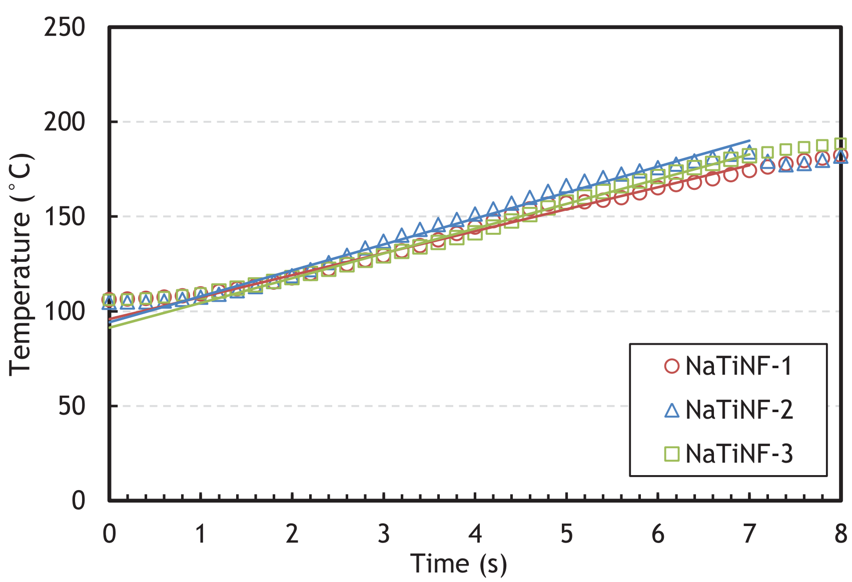
The temperature increment of reaction at the initial period of Na and NaTiNF has been obtained from every reaction cases (Fig. 7). The standard error of obtained values has been established in Table 2. Increment rate of Na case is 17.45 ˚C/s at the beginning of the reaction and it soon reaches to the highest temperature of 241 ˚C (Table.2).

Table II. Result of SVR

SVR case	Mass	Initial Temperature	Highest Temperature	Temperature Increment	
Na	0.2064 g	105.6 (±0.10) ˚C	≈241 (±6) ˚C	(a)	17.45 (±0.93) ˚C/s
NaTiNF	0.2114 g	105.4 (±0.24) ˚C	≈215 (±6) ˚C	(b-1)	12.78 (±1.09) ˚C/s
				(b-2)	2.65 (±0.49) ˚C/s



(a)



(b)

Figure 7. Temperature increment at the initial period in (a) Na, (b) NaTiNF

As it mentioned above, temperature of Na case is exponentially increased, but NaTiNF case has two different increase rates: 12.78 ˚C/s at the beginning (Fig. 6 b-1) and 2.65˚C/s after 13s (Fig. 6 b-2). The temperature increment rate of NaTiNF is reduced to 63% of that of Na case. This distinctive reaction characteristic of NaTiNF is the same as that of the previous SWR experiment [6]. The SVR occurs mainly on the liquid Na surface in which water molecules contact with sodium atoms. Therefore, dispersed Ti NPs on the reaction surface is considered to control the reaction rate at the beginning of reaction and affect as reaction continues.

To demonstrate the behavior of the surface reaction of Na and NaTiNF, high-speed camera records the reaction at the surface with 500 frame/s during SVR. Reaction begins at 0s and becomes vigorous as reaction continues (Fig. 8). In the Na case, Na surface shows silver color as its original characteristic at time 0s. As reaction begins at the surface of Na along the shape of sphere, pure sodium meets water vapor and generates sodium hydroxide that mixed with water showing white color, sodium lose its silver color though at 0.14s in Fig. 8. The behavior of NaTiNF is different from Na case at 0.14s. In the case of Na, the surface reaction already begins by producing reaction products. However, similar surface reaction like in the case of Na has not been observed in the case of NaTiNF. The surface of NaTiNF remains stable while the water vapor has been continuously injected. It seems that sodium that are not interacted with the Ti NPs starts to react with water. Ti NPs settled on the surface of NaTiNF blocks the contact between sodium and water [6]. Water hardly reacts with sodium near by the NPs, but reacts with sodium that has not been interacted with Ti NPs. This restricted reaction path mitigates reaction rate of NaTiNF at the very beginning reaction period. This results in the lower temperature increment in NaTiNF as Fig. 6 (b-1).

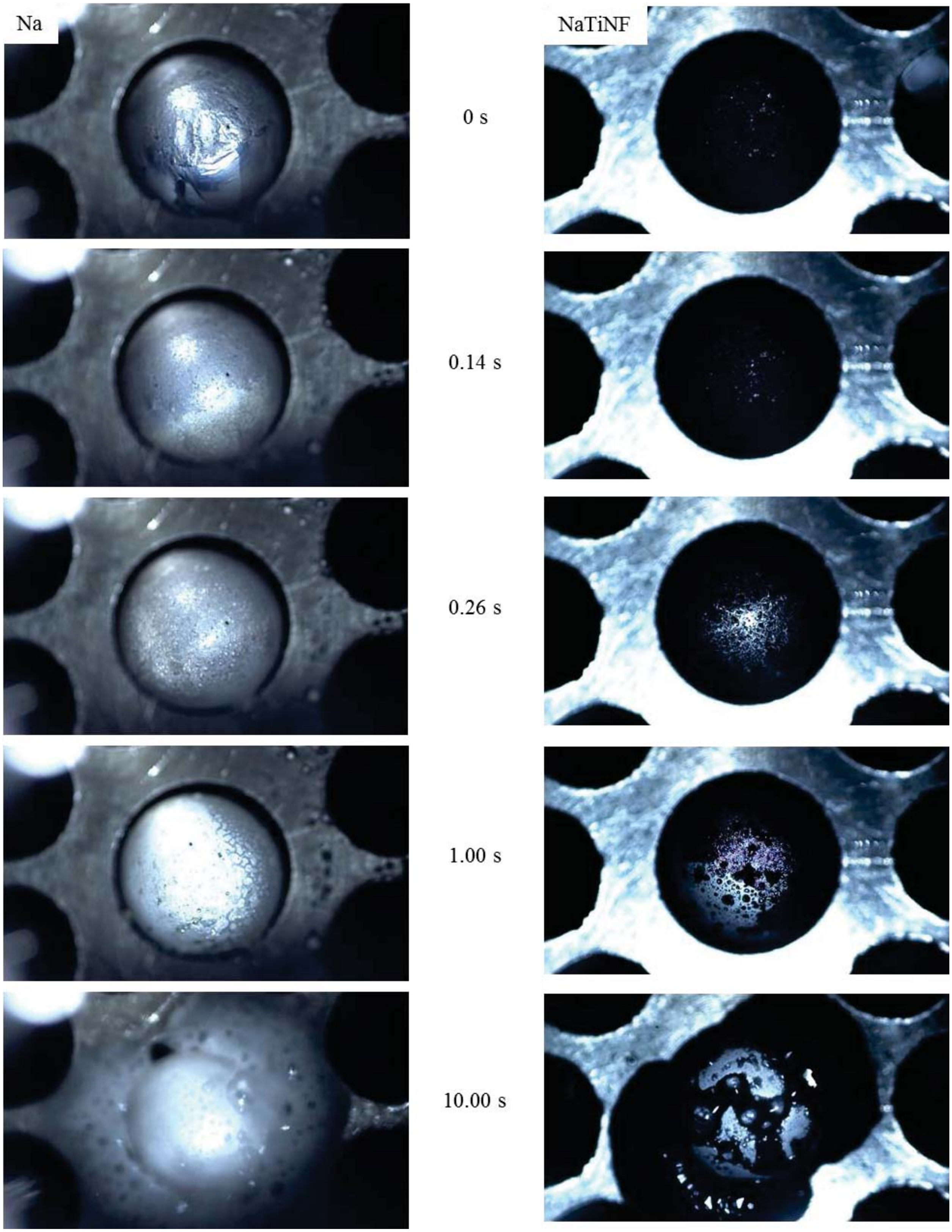


Figure 8. High speed images of SVR.

Moreover, it is suspected that as reaction continues, Ti NPs in NaTiNF remains above liquid Na with reaction products (NaOH + H_2O). These remained Ti NPs and reaction products suspected to protect reactant surface from the contact with water vapor. Therefore, the reaction products with Ti NPs covering the reaction surface of NaTiNF can reduce the temperature increment rate (Fig. 6 b-2) as the reaction continues in NaTiNF case. However the exact mechanism of this reaction behavior in NaTiNF should be closely observed by more accuracy surface visualization.

3. DISCUSSION

As it mentioned previously [6, 9] that if Ti NPs on liquid sodium surface interrupt the contact between sodium and water molecules, the concentration of NPs on the reaction surface will be a key factor that can effectively suppress the chemical reactivity of liquid sodium with water. As the concentration of NPs in liquid sodium increases, the reaction rate of liquid sodium can be reduced as well. The effect of the concentration of NPs on sodium reactivity should be studied for verifying the role of NPs in suppressing the reactivity of sodium. Moreover, if any chemical interaction between NPs and sodium atoms is the dominant factor that can suppress the reactivity of sodium, the other material can be the candidate for the dispersed NPs. Based on a nanoparticle-sodium cluster model in the previous work, titanium has been considered as the strongest atomic bond with sodium atom than other transition materials [1]. However the effect of other material in SWR has not been verified. For the deep understanding of the interaction between NPs and sodium atoms, the various NPs should be investigated in the future.

The consideration of NaTiNF as an alternative coolant for SFR design is still doubtful for a real accident scenario. This suppression effect of NaTiNF has only performed in lower temperature than the real operating condition and in well-defined reaction situation. To reproduce SWR in a tube rupture accident situation, pressurized water should be injected into liquid sodium flow. The reaction characteristics must be quite complex in real situation. However this study indicates the possibility of suppressing the explosive reactivity of liquid sodium in a fundamental step. Moreover, the stability of using nanoparticles in the utility systems in a power plant is also under the consideration.

4. CONCLUSIONS

NaTiNF (liquid Na based Titanium Nano Fluid) has been produced to mitigate the chemical reactivity of liquid sodium. Suppressed chemical reactivity of NaTiNF is experimentally demonstrated by the reaction between NaTiNF with water vapor. Temperature increment rate of NaTiNF resulted by exothermal reaction with water vapor is 12.78 (±1.09) °C/s at the beginning of reaction which is lower than that of Na with 17.45 (±0.93) °C/s. This suppressed reactivity is almost 63% of Na-water vapor reaction case. The distinct temperature increment of NaTiNF shows two different rates. The visualization of surface reaction using high-speed camera presents that the surface of NaTiNF remains stable while surface of Na becomes turbulent due to the reaction with water vapor. These results indicate that dispersed Ti NPs in NaTiNF suppress the chemical reactivity of liquid sodium in the reaction.

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