Experimental Study of Na based Titanium Nanofluid-Water Reaction

Gunyeop Park [a], Soo Jae Kim [a], Hyun Soo Kim [b], Sun Ryung Oh [b], Hyun Sun Park [b*], Moo Hwan Kim [bc], Jehyun Baek [a]
[a]*Department of Mechanical Engineering, POSTECH, Pohang 790-784, Korea*
[b]*Division of Advanced Nuclear Engineering, POSTECH, Pohang 790-784, Korea*
[c]*Korea Institute of Nuclear Safety, Yuseong, Daejeon 305-338, Korea*
[*]*Corresponding author: hejsunny@postech.ac.kr*

1. Introduction

Use of liquid sodium (Na) in SFR brings high cooling efficiency, but this strategy is risky because when liquid Na contacts water, Sodium-Water Reaction (SWR) occurs. SWR accident increases system pressure rapidly and this threatens the safety of nuclear power plant systems. 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 KALIMER-600, a sodium-cooled fast reactor designed by KAERI, thermal energy is transported from high-temperature liquid Na (526 °C at 0.1 MPa) to low-temperature water (230 °C at ~19.5 MPa) through a heat exchanger [6, 7]. If any leakage or rupture occurs during the operation of this heat exchanger, highly pressurized liquid water can penetrate into the liquid Na channels; this contact should instantly cause SWR. 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.

To reduce this strong chemical reaction phenomena between Na and water, some we have focused on suppressing the chemical reactivity of liquid Na by dispersing nanoparticles (NPs). We have suggested Na-based Titanium nanofluid (NaTiNF) which containing Ti NPs (<100nm) in liquid Na [8, 9]. We have experimentally demonstrates the suppressed reactivity of NaTiNF when it contacts with water. Moreover, theoretical approach to the chemical interaction between Na atoms and Ti NPs has been investigated by ab-initio calculation [13].

For the real application of NaTiNF, the pressure change induced by NaTiNF-water reaction is compared with Na-water reaction in the present study. NaTiNF contains 100nm of Ti NPs at 0.2 vol. %. The reaction rate of NaTiNF-water reaction is also investigated as reaction temperature increases. Sodium-water vapor reaction (SVR) will occur when an SWR accident occurs in SFR. In this manner, NaTiNF-water vapor reaction is experimentally performed for ensuring the suppression of chemical reactivity of NaTiNF in contact with water vapor.

2. Experimental arrangement

2.1 NaTiNF-water reaction

For an SWR, the experimental set-up is the as previous study [8-10, 12]. The reactor is consisted of the crucible sodium container, water storage, pressure sensor line, vacuum pump line and thermocouple (Fig. 1). The reactants (Na or NaTiNF) are stored in the crucible which is perfectly sealed. The reactor is heated by a conduction heater. When the reactor temperature reaches a target temperature (reaction temperature T_R = 104, 120, 150 ˚C), the reactor is detached from the heater and evacuated by the vacuum pump. To trigger the reaction, a valve between the reactor and a water storage tank open to inject water into the reactor by low pressure inside it. Absolute pressure transducer determines the pressure change during the reaction. The change of pressure in reactor represents the reaction phenomena of SWR. In this experiments, approximately 0.2g of Na or NaTiNF reacts with 2.5ml of distilled water.

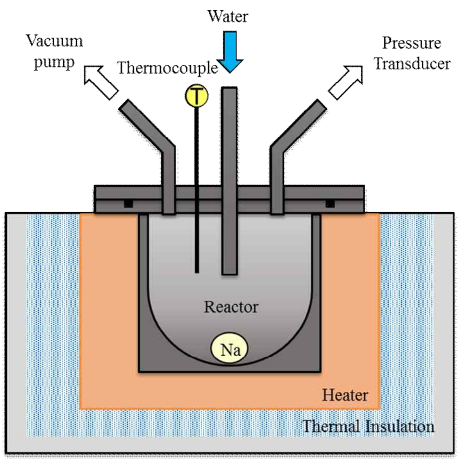

Fig. 1. The reactor is designed to inject a distilled water to liquid Na to trigger an SWR at T_R = 104, 120, 150 °C.

2.2 NaTiNF-water vapor reaction

The reactor for Sodium-water vapor reaction (SVR) is designed water vapor flows over the surface of Na or NaTiNF to occur the surface reaction [11]. A steam generator supplies water vapor at 100 ˚C into the reactor through the bottom of it. Liquid Na or NaTiNF is stored on the intermediate plate (Fig. 2). Excess of water vapor flows and contacts with liquid specimen, then surface reaction occurs. The gas reaction product (H_2) and rest of water vapor are vented out to environment. K-type thermocouple directly contacts with the reactant and measures the temperature change during the reaction. As an SWR experiment, 0.2g of Na or NaTiNF (containing 0.2 vol. % of Ti NPs) reacts with water vapor at T_R = 105 ˚C. The temperature changes in Na-water vapor and NaTiNF-water reaction are compared.

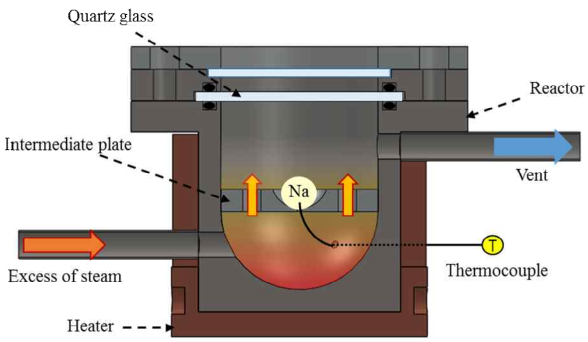

Fig. 2. As excess of water vapor flows to upper, liquid Na continuously reacts with it, then temperature of the specimen increases until reaction completion.

3. Results

3.1 Pressure change in NaTiNF-water reaction

Pressure change of Na-water reaction is compared with that of NaTiNF-water reaction. Pressure begins to increase when reaction occurs at 1s in Fig. 3. At T_R=104 ˚C, pressure rapidly increase in both Na and NaTiNF case, but more rapidly increases in Na-water reaction. Na shows higher maximum pressure Pmax (blue dot lines in Fig 3) than NaTiNF.

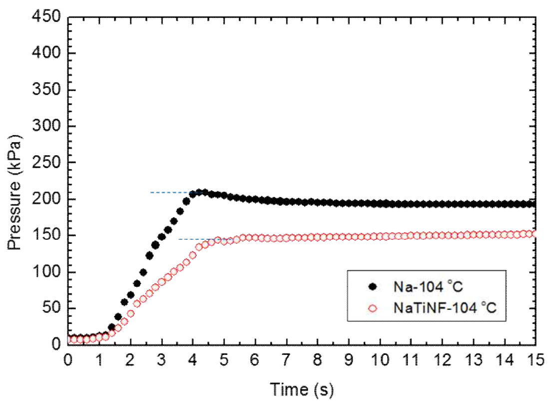

Fig. 3. Na or NaTiNF-water reaction at T_R = 104 °C.

At T_R=120 ˚C, reaction phenomena is similar to previous one. Although Pmax in both cases are higher than that at 104 ˚C, pressure in Na case increases faster than in NaTiNF case (Fig. 4). Pmax is still higher in Na case than NaTiNF case.

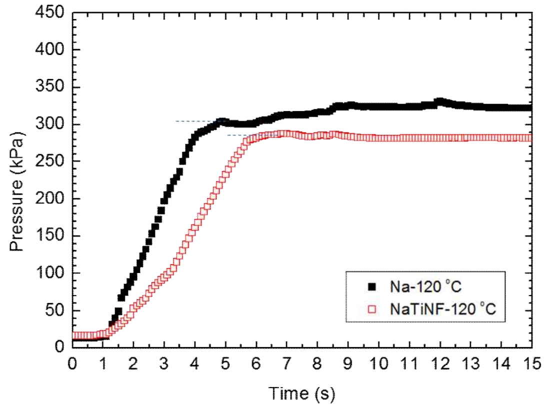

Fig. 4. Na or NaTiNF-water reaction at T_R = 120 °C.

At T_R=150 ˚C, Pmax in Na-water reaction becomes much higher than previous T_R (Fig. 5). It increase with T_R increases. In contrast to Na case, Pmax in NaTiNF-water reaction becomes much lower than reaction at T_R=120 ˚C. The distinct pressure change of NaTiNF should be induced by slow reaction mechanism.

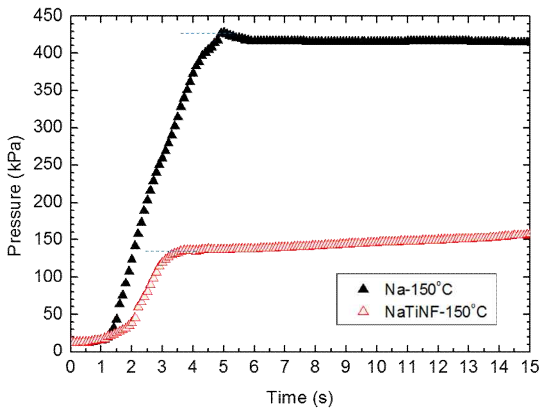

Fig. 5. Na or NaTiNF-water reaction at T_R = 120 °C.

To investigate the distinct reaction phenomena of NaTiNF at T_R = 150 °C, moles of hydrogen generation (N_{H2}) during the reaction is obtained by the ideal gas law in order to eliminate the volume expansion by temperature of reactor and released reaction [10]. The hydrogen generation during Na-water reaction at T_R =150 °C is compared with NaTiNF until reaction completion (Fig. 6). Na shows instant reaction completion in a short time, but NaTiNF shows several step reactions to complete the reaction. It takes dramatically longer time than Na. The step reaction shown in Fig 6 can be induced by the slow reaction characteristic of NaTiNF that control the formation of oxide layer on the surface of NaTiNF during the reaction [10, 12].

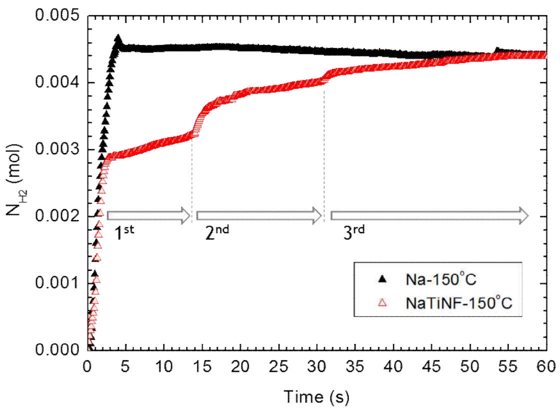

Fig. 6. An instant reaction completion in Na, but NaTiNF shows step reaction until reaction completion.

3.2 Reaction rate of NaTiNF-water reaction

The number of moles of H_2 (N_{H2}) during NaTiNF-water reaction at T_R = 104, 120 and 150 ˚C is compared to determine the rate of reaction (Fig. 7). The number of moles of (N_{H2}) is normalized by the final number of moles of H_2 (N_{final}) at reaction completion.

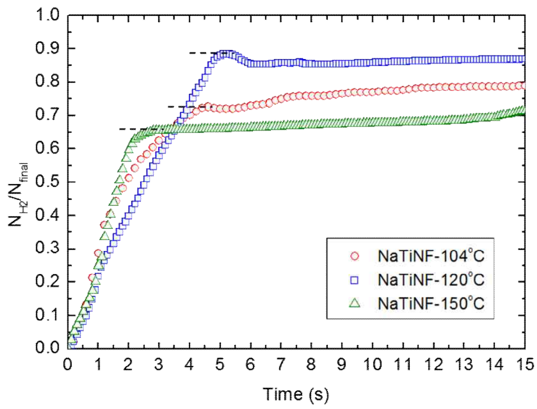

Fig. 7. Normalized H_2 generation regarding to total H_2 during NaTiNF-water reaction at T_R = 104, 120, 150 °C.

The peak point (black dot line in Fig 7) of NaTiNF at T_R = 120 °C becomes higher than T_R = 104 °C as temperature increase. However as we verified previously, peak point at T_R = 150 °C becomes lower than that at T_R = 120 °C. The distinct reaction phenomena of NaTiNF is result of reaction mechanism [10]. We need to verify the speed of NaTiNF-water reaction.

To determine the reaction rate of SWR, a parabolic law is normally used. The number of moles of H_2 (N_{H2}) is determined by the rate law in the rate-determining step [14]. We have modified the rate law for SWR. k (s^{-1}) is rate constant and t (s) is time.

$$[N_{H2}]^2 = kt \quad (1)$$

N_{H2} is normalized by N_{final} at reaction completion.

$$[N_{H2}/ N_{final}]^2 = kt \quad (2)$$

The reaction rate is defined from beginning of reaction to peak point. At T_R = 104 °C, the reaction rate of Na-water reaction is higher than that of NaTiNF as show in Fig. 8. The suppressed NaTiNF-water reaction clearly shows that it is half as slow as Na-water reaction.

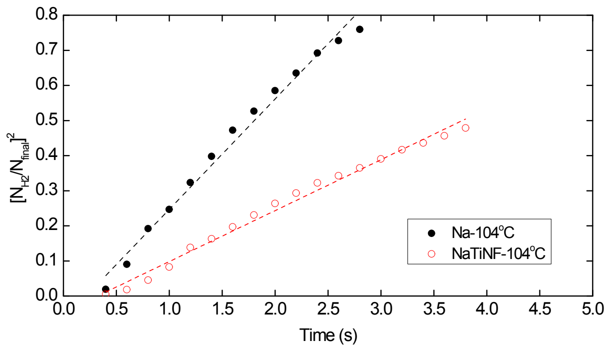

Fig. 8. k of Na is 313.9 (± 19.4) ×10^{-3} (s^{-1}) while k of NaTiNF 144.4 (± 16.0) × 10^{-3} (s^{-1}).

The reaction rate of NaTiNF is compared as T_R increases. Although peak point of NaTiNF at T_R = 150 °C is lower than T_R = 120 °C (Fig. 7), the reaction rate at T_R = 150 °C shows higher reaction rate than T_R = 120 °C (Fig. 9). Rate constant of NaTiNF-water reaction increases with T_R increases. This deduces that the reaction becomes vigorous as reaction temperature increases, but the reaction mechanism of NaTiNF at T_R = 150 °C becomes different from T_R = 104, 120 °C as reaction continuous.

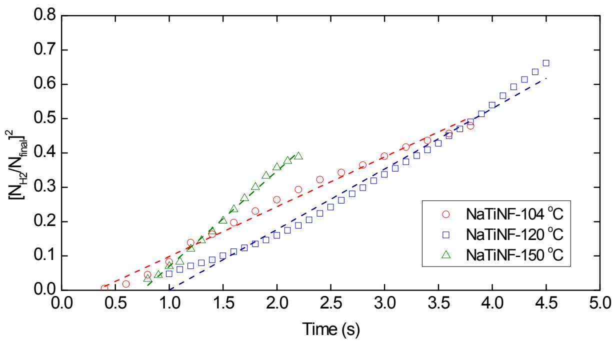

Fig. 9. k of NaTiNF increases with T_R; 144.4 (± 16.0) × 10^{-3} at T_R =104 °C, 188.8 ± (10.0) × 10^{-3} at T_R =120 °C and 278.4 (± 10.1) × 10^{-3} at T_R =150 °C.

3.3 NaTiNF-water vapor reaction

SVR is relatively slower reaction than SWR due to low density of water vapor. We determines the reactivity of NaTiNF by temperature increase due to exothermic chemical reaction of SVR. Approximately 0.2g of Na or NaTiNF is engaged in reaction with water vapor. NaTiNF contains 0.2 vol. % of Ti NPs as previously. The T_R of specimen is 105 ˚C.

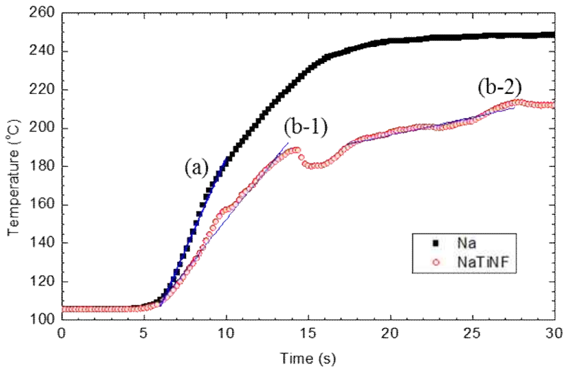

Fig. 10. Temperature change of Na or NaTiNF in reaction with water vapor. Reaction is triggered at 5s.

Temperature increases with the beginning of reaction at 5s in Fig. 10. The increase in temperature between Na and NaTiNF is clearly different. Temperature in Na-water reaction initially increases 19.2 °C/s (Fig. 10a) to reach the highest temperature ~248 °C. In contrast to Na, temperature change in NaTiNF-water vapor reaction initially shows 10.6 °C/s (Fig. 10b-1) and soon becomes 1.9 °C/s (Fig. 10b-2) until reaction completion. The highest temperature in NaTiNF is approximately ~213 °C which is lower than Na case. This difference in the highest temperature between Na and NaTiNF deduces the difference in heat disposal mechanism through reaction products that covering the specimen [11]. This result demonstrates the suppressed chemical reactivity of NaTiNF in the reaction with water vapor once again.

4. Conclusions

In the basic step for reducing risk of an SWR in SFR, we have experimentally verified the suppressed chemical reactivity of liquid sodium using Ti NPs through SWR and SVR experiments. In SWR, Na based titanium nanofluid (NaTiNF) shows lower pressure change than Na. As T_R increases, Pmax in Na-water reaction increases while NaTiNF does not. The reaction rate of NaTiNF shows twice slower than that of Na. In SVR, NaTiNF shows slower temperature increase than Na. The distinct temperature change of NaTiNF shows two different rate of temperature increase. These remarkable results demonstrate the reducing potential possibility of SWR accident in SFR system.

ACKNOWLEDGEMENT

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MEST) (NRF-2010-0018679).

REFERENCES

[1] R.H. Jones, H.J. Williams, J.A. Murphy, NaK-water reactions test, Atomic power development associates, INC. Detroit, Michigan, AECU-3193, 1956.
[2] D.D. Adams, G.J. Barenborg, W.W. Kendall, Evaluation of the sodium-water reaction in heat transfer systems, Knolls Atomic Power Lab., KAPL-P-1512, pp. 92-105, 1956.
[3] J.A. Ford, Literature review of sodium-water reactions, Atomic Power Development Associates, Inc., Detroit, Michigan. Subcontract No. 1. AEC AT(11-1)-1280, 1965.
[4] A.G. Newlands, W.D. Halstead, The reaction between water droplets and molten sodium, Int. J. Heat and Mass Transfer, Vol. 21, p. 897-903, 1978.
[5] D. Saphier, D., A kinetic model of sodium-water reaction applied to dynamic simulation of leak detection in the core components test loop, Illinois: Argonne National Laboratory. ANL-75-22, 1978.
[6] D. Hahn, Y. Kim, C.B. Lee, S. Kim, J.H. Lee, Y.B. Lee, B. Kim, H.Y. Jeong, Conceptual design of the sodium-cooled fast reactor Kalimer-600, Nuclear Engineering and Technology, Vol. 37, p. 193-206, 2007.
[7] Y. Kim, Y.B. Young, C.B. Lee, J. Chang, C. Choi, Design concept of advanced sodium-cooled fast reactor and related R&D in Korea, Science and Technology of Nuclear Installations, Vol. 2013, 2013.
[8] G. Park, S.J. Kim, M.H. Kim, Reduction of chemical activity of liquid sodium by Ti nanoparticles, Transactions of the Korean Nuclear Society Autumn Meeting, Oct. 24-25, 2013, Gyeongju, Korea.
[9] G. Park, S.J. Kim, M.H. Kim, H.S. Park, Experimental study of the role of nanoparticles in sodium–water reaction, Nuclear Engineering and Design, Vol. 277, p. 46-54, 2004.
[10] G. Park, S.J. Kim, H.S. Park, M.H. Kim, J. Baek, Reaction rate of Na based titanium nanofluid with water, J. Nuclear Science and Technology, 2015a. (online published)
[11] G. Park, S.J. Kim, H.S. Park, M.H. Kim, The effect of titanium nanoparticles on Na-water vapor reaction at 105 °C, Nuclear Engineering and Design, 2015b. (Accepted in July)
[12] G. Park, S.J. Kim, H.S. Park, M.H. Kim, J. Baek, Change of pressure during Na-water reaction using titanium nanoparticles, Nuclear Engineering and Technology, 2015c. (Submitted)
[13] S.J. Kim, G. Park, M.H. Kim, H.S. Park, J. Baek, A theoretical study of Ti nanoparticle effect on sodium water reaction: Using ab initio calculation, Nuclear Engineering and Design, Vol. 281, p. 15-21, 2015.
[14] L.F. Epstein, Metal-water reactions, VI. Analytical formulations for the reaction rate, Califonia: General Electric Co. Vallecitos Atomic Lab., GEAP-3272, 1959.