General corrosion properties of modified PNC1520 austenitic stainless steel in supercritical water as a fuel cladding candidate material for supercritical water reactor

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Abstract. The Super-Critical Water-cooled Reactor (SCWR) has been designed and investigated because of its high thermal efficiency and plant simplification. There are some advantages including the use of a single phase coolant with high enthalpy but there are numerous potential problems, particularly with materials. As the operating temperature of supercritical water reactor will be between 280 °C and 620 °C with a pressure of 25MPa, the selection of materials is difficult and important. Austenitic stainless steels were selected for possible use in supercritical water systems because of their corrosion resistance and radiation resistance. The PNC1520 austenitic stainless steel developed by Japan Atomic Energy Agency (JAEA) as a nuclear fuel cladding material for a Na-cooled fast breeder reactor. The corrosion data of PNC1520 in supercritical water (SCW) is required but does not exist. The purpose of the present study is to research the corrosion properties for PNC1520 austenitic stainless steel in supercritical water. The supercritical water corrosion test was performed for the standard PNC1520 (1520S) and the Ti-additional type of PNC1520 (1520Ti) by using a supercritical water autoclave. Corrosion tests on the austenitic 1520S and 1520Ti steels in supercritical water were performed at 400, 500 and 600 °C with exposures up to 1000h. The amount of weight gain, weight loss and weight of scale were evaluated after the corrosion test in supercritical water for both austenitic steels. After 1000h corrosion test performed, the weight gains of both austenitic stainless steels were less than 2 g/m² at 400 °C and 500 °C. But both weight gain and weight loss of 1520Ti were larger than those of 1520S at 600 °C. By increasing the temperature to 600 °C, the surface of 1520Ti was covered with magnetite formed in supercritical water and dissolution of the steel alloying elements has been observed. In view of corrosion, 1520S may have larger possibility than 1520Ti to adopt a supercritical water reactor core fuel cladding.

1. Introduction
The concept of Super-Critical Water-cooled Reactor (SCWR) has been well developed world-widely, designed and investigated world-widely because of its high thermal efficiency and plant simplification. The supercritical water cooled reactors are considered as one of the expecting future high efficiency systems with some advantages. They include many options, for example, thermal neutron spectrum.

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fast neutron spectrum, high thermal efficiency exceeding 40%, minimum researching and developing costs, the matured technologies of Light Water Reactors (LWRs) and supercritical pressure fossil power, thermal/fast hybrid neutron spectrum, pressure tube type, pressure vessel type, and so on [1-3]. There are some advantages including the use of a single phase coolant with high enthalpy. Supercritical Water (SCW) has never been used in nuclear power applications. There are numerous potential problems, particularly with materials [4-7]. As the operating temperature of supercritical water reactor will be between 280°C and 700°C with a pressure of 25MPa, the selection of materials is difficult and important. The design provides a simplified, reduced volume system with high thermal efficiency. The increase of operating temperature and pressure as compared to current state-of-the-art Boiling Water Reactor (BWR) and Pressurized Water Reactor (PWR) designs will make it difficult to realize the fuel cladding for supercritical water reactor. Water in the supercritical phase exhibits that its property is significantly different from that of liquid water below the critical point. Its density largely depend on temperature and pressure from less than 0.1 g/cm³ values similar to that of water below the critical point. Saito et al.[8] evaluated by the thermal calculation that the value of the density in supercritical water will be 90% reduced to water of room temperature. The pH value in supercritical water will increase to be about 12 at neutral at 500°C. These conditions allow the properties of supercritical water, such as the ion product heat capacity and dielectric constant to vary. In addition, the material for the supercritical water reactor core will be exposed with fast neutron irradiation. The condition is so severe for fuel claddings and structural materials to be faced with the problems of:

- Corrosion
- Irradiation-Assisted Stress Corrosion Cracking (IASCC)
- Swelling
- High temperature strength …. 

The dielectric constant of supercritical water will be decreased (1/20 less than that of room temperature) [8]. The eluted metal elements will be hard to be ionized in supercritical water. As Zircaloy-4, which is used as a cladding for PWR, is insufficient and corrosive at higher than 400°C, the several candidate materials for supercritical water reactor cladding have been screened [9-10]. Austenitic stainless steels have some advantages in cladding materials for supercritical water reactor core.

Austenitic stainless steels were selected for possible use in supercritical water systems because of their corrosion resistance and radiation resistance. One solution is PNC1520 austenitic stainless steel that has been developed by Japan Atomic Energy Agency (JAEA) as a nuclear fuel cladding material for a Na-cooled fast breeder reactor and is based on SUS316L to be modified for the fast neutron irradiation up to 100 dpa. Austenitic Fe-base steels were selected for possible use in supercritical water systems because of their corrosion resistance and radiation resistance. But the corrosion data of PNC1520 in supercritical water is required but does not exist.

The purpose of the present study is to investigate the corrosion behaviour for the standard PNC1520 austenitic stainless steel (1520S) and the Ti-additional modified PNC1520 (1520Ti) in supercritical water.

2. Experimental

2 types of PNC1520 were fabricated by Kobelco Research Institute Inc.: 1520S and 1520Ti. 1520S is standard type PNC1520 austenitic stainless steel for a Na-cooled fast breeder reactor. 1520Ti is the modified trial austenitic stainless steel based on 1520S to improve the strength at the grain boundary. The chemical composition of specimens is as follows: for 1520S (Cr: 15.11, Ni 19.88, Ti 0.23, C 0.063, Mn 1.75, Mo 2.51, Si 0.87 and Fe balance) and 1520Ti (Cr: 15.19, Ni 19.85, Ti 0.42, C 0.060, Mn 1.75, Mo 2.50, Si 0.87 and Fe balance [wt%]) respectively.
The supercritical water corrosion test was performed using 1520S and 1520Ti, which are the first trial production material as supercritical water corrosion test material. The present study has evaluated weight gain $W_G$, weight loss $W_L$ and weight of scale $W_S$ for 1520S and 1520Ti austenitic stainless steels in Supercritical Water.

When referring to an equation, (1), (2) and (3),

$$W_G = \frac{m_1 - m_0}{A_0}$$  \hspace{1cm} (1)

$$W_L = \frac{m_0 - m_d}{A_0}$$  \hspace{1cm} (2)

$$W_S = \frac{m_1 - m_d}{A_0}$$  \hspace{1cm} (3)

where $m_0$ is the sample weight before corrosion, $m_1$: the sample weight after corrosion, $m_d$: the sample weight after removing scales and $A_0$: the superficial area before corrosion test.

The weight before the corrosion test $m_0$ was measured to evaluate the weight gain, the weight loss and the weight of scale. The weights of pieces were measured, the weight after corrosion $m_1$, an test to $A_0$ for the weight after $m_1$ and removing scale processing, weight gain ($W_G$) and corrosion loss ($W_L$), and the oxide/layer weights ($W_S$) are expressed with the formula (1)-(3), respectively.

The weight loss $W_L$ is defined as the weight difference between the weight before corrosion and after removing scales by AP-AC method. The AP-AC method to remove the corrosion layer on the specimen should be used by 10 wt% KMnO₄ and NaOH respectively. The operation in which it was continuously immersed into 10 wt% mixed boil solution oxalic acid ammonium (COONH₄)₂ was repeated in up to 3 times of the ranges, and operation was repeated until it was judged by observation that the scale was removed.

The materials to fabricate ingots were melted by arc-melting furnace. The heat treatment of the materials in the present study was solution treatment at about 1150 $^\circ$C for 3 times with quenching. After the heat treatment, materials were machined into specimens. The test materials were first processed into the piece form of the corrosion tests as shown in Fig.1, which dimensions about 3x10x15 mm³ as shown in Fig. 2 and their average weight is about 4 g.
Their surfaces were wet-polished by Emery papers (#320-#1000). The batch type autoclave with a compressor to regulate its pressure (25MPa, ≤600 ºC, ≤1000h) was performed. 2 types of materials: 1520S and 1520Ti were corroded in supercritical water at 400, 500 and 600 ºC for 100, 200, 500 and 1000h. The pressure and temperature values were indicated and recorded by the system connected to manometer and thermo couples. The temperature of the water was controlled to the same between top and bottom of the autoclave. Table 1 shows the corrosion conditions of 1520S and 1520Ti in supercritical water of 25 MPa.

| Conditions                  |      |
|-----------------------------|------|
| Corrosion pressure [MPa]    | 25   |
| Corrosion temperature [ºC]  | 400, 500, 600 |
| Corrosion time [h]          | 100, 200, 500, 1000 |
| Materials                   | 1520S, 1520Ti |

The sample holder was made of hastelloy C276 and pretreated with its surface oxidation for insulation to prevent electrons from moving between sample holder and specimens. Thus, the corrosion test in supercritical water environment was presented in Table I with the piece of a test after washing and degreasing with ethanol and acetone before the supercritical corrosion test. The corrosion tests that four specimens as 1 set to each test conditions were performed. The four corrosion specimens for each material were immersed in supercritical water. The corrosion behaviour was evaluated through their weight changes. Water chemistry conditions were set for the corrosion tests in severe ways for corrosion times and corrosion temperatures with the initial oxygen concentration of about 1.72 wtppm. The specimens after corrosion test were processed to remove the oxide layer with the AP-AC method [5]. The weight of oxide layer, which produced on the sample surface by supercritical water corrosion, was evaluated by the weight after the corrosion test and the removing process. The average of weight change before and after the corrosion test was measured. After removing scale by the AP-AC processing, the weight gain \( W_G \), the weight loss \( W_L \) and the oxide/layer weight \( W_S \) were estimated. The weight gain \( W_G \) is defined as the sum of the weight increase caused by oxidization and the weight decrease by elusion. It is impossible to measure the true weight increase
and the true weight decrease for the corroded specimens. The weight changes before and after the corrosion tests could be measured. Weight of specimen before corrosion test is expressed by the value of $m_0$. The weight of the specimen after corrosion is expressed by the value of $m_1$. The value of $W_G$, $W_L$ and $W_S$ were standardized by the surface area of specimens. At 600 $^\circ$C, both austenitic stainless steels showed larger weight gain than lower temperatures. The weight gain of 1520Ti increased at 600 $^\circ$C significantly. Below 500 $^\circ$C, the weight gain of 1520Ti and 1520S were less than 3 g/m² for 1000h. The weight gain means the sum of oxidation and elusion. The increase of weight gain implies the amount of oxidation is more than that of elusion.

The corrosion increase is weight change including both increase in weight by oxide layer formation and weight reduction by dissolution, and global weight loss is the amount of dissolution which began to melt into the solvent from the piece surface of an test. The oxide/layer weights are obtained from the weight change before and after removing scale processing. Electrolysis etching was given and grain boundary susceptibility was evaluated, after making the surfaces treated by mechanical polish in the Emery papers (#320, #600 and #1000). Phase observation and SEM observation were performed.

After corrosion test, the surfaces of some specimens were mechanically polished from Emery paper (#320-#1000, buff 3 μm, 0.25 μm, 0.05 μm) to remove the scale and affected area and electrically polished from 1 A/cm² 40 V in 10 wt% oxalic acid to observe the susceptibility for their grain boundaries.

The surface observation and the cross-sectional observation were performed by the scanning electron microscope (SEM) after the corrosion test. It performed evaluation of their surface form changes and a structural change. It is necessary to evaluate about the relation of the test time and the corrosion action with which the corrosion test was presented.

3. Results and discussion
The weight gain by corrosion was evaluated for supercritical water up to 1000h in Fig. 3. The weight change is sum of both increase in weight by oxide layer formation, and weight reduction by elusion.

![Graph](image)

**Fig. 3:** Weight gain as a function of corrosion time for 1520S and 1520Ti exposed to supercritical water at 400, 500, 600 $^\circ$C, <1000h.
As to the weight loss of both 1520S and 1520Ti, there is a threshold temperature between 500 °C and 600 °C for corrosion increase as shown in Fig. 4. The weight loss means the amount of the corroded layer without elusion. Saito et al. calculated the dielectric constant of supercritical water. Thermodynamics calculation provides one of the methodology for the fundamental clarification and expectation of corrosion product behaviour in high-temperature water, such as supercritical water, where it is difficult to measure the experimental data because of extremely high temperature and high pressure.

![Graph](image)

**Fig.4:** Time dependence of weight loss for 1520S and 1520Ti at 400, 500 and 600 °C in supercritical water of 25MPa

In order to elucidate the dissolution/deposition behaviour of corrosion products in supercritical-water-cooled reactor coolant, chemical thermodynamics calculation was carried out by them. Above the Critical Point, the ε turns to be 1/20 less than that of room temperature. The water gradually becomes nonpolar solvent. At room temperature, the ions were stabilized in the water by its polarity. But in supercritical water, the effect will be reduced. The time dependency of the weight of scale of both 1520S and 1520Ti was almost the same. As shown in Fig. 5, the weight of scale showed that as the temperature increased, the weight of scale increased. The corrosion condition in supercritical water is in thermodynamic equilibrium state. The weight of scale expresses the weight of the corroded and eluted part of the specimens to be removed by AP-AC method. Fig.6 showed that the corrosion rate of 1520Ti at 600 °C is different from those of 1520S at 400-600 °C and of 1520Ti at 400 and 500 °C. The corrosion rate was extrapolated by the corrosion data for 1000h. On the assumption that the limit of corrosion for cladding in supercritical water reactor is 10% of the thickness of wall, 40μm, the corrosion rate for cladding material should be less than 12μm/year. The corrosion rate of 1520Ti at 600 °C is undesirable.
Fig. 5: Time dependence of weight of scale for 1520S and 1520Ti at 400-600 °C in supercritical water.

Fig. 6: Corrosion temperature dependence of dissolution for 1520S and 1520Ti evaluated by 1000h.

As shown in Table 2, the corrosion-resistant characteristic of 1520S keeps at 500 °C. As the corrosion temperature increased from 400 °C to 600 °C, the corrosion on their surfaces made progress. At 400 °C, the linear polishing traces were clearly observed, they were almost disappeared at 500 °C and they...
were not observed completely at 600 °C. The island-like corrosion products on their surfaces were observed at 400 and 500 °C. The observed weight gain of 1520Ti samples at 600 °C is attributed to the morphology changes that showed the grains of magnetite made crystalline growth.

Table 2. SEM morphologies of the 1520S and 1520Ti samples after exposure to 25 MPa SCW at 400, 500 and 600 °C for 1000 h (SEI, 400). The polishing lines were disappeared because of corrosion as the corrosion temperature increased from 400 °C to 600 °C.
Table 3. SEM morphologies of 1520S and 1520Ti on the surfaces of the specimens after 1000h exposure in supercritical water (25MPa, 400, 500 and 600 °C, □ 4000). The effect of time and temperature on oxide growth in 1520S and 1520Ti austenitic stainless steels can be seen in those figures. The grain on the surface of the sample of 1520Ti at 600 °C shows facet and steps.
Shown in Table 3, the surface of 1520S 600°C was covered with the fine grains of 100-500 nm. The surface of 1520Ti corroded at 600°C showed the corroded facet of magnetite confirmed by XRD result. Grains seemed to be growing grain morphology for 1000 h as they have steps. The oxide layer of the surface of the specimen was identified as magnetite by XRD measurement. The surface of 1520S corroded at 400-500°C was the mixture of magnetite and Fe-Cr-Ni, that at 600°C was Fe-Cr-Ni and Cr₂O₃ phases, where the XRD peaks of the magnetite were weak. The dominant phase of 1520Ti corroded at 400-500°C was that of magnetite and Fe-Cr-Ni. The phase at 600°C was that of magnetite. The magnetite phase Fe₃O₄ was formed on the surface of 1520Ti at 600°C by XRD results. Potential-pH (E-pH) diagram drawn by experimental data, which exhibited the effect of temperature and pressure on the stability of oxide in the supercritical water reactor core region, was not available for metal/water system in the supercritical water condition. Saito et al. carried out thermodynamic calculation to evaluate the potential-pH diagrams for metal/supercritical water system, diagrams of which have been widely used in LWR water chemistry to consider the corrosion product behaviour [8-10]. They calculated potential-pH for Fe/H₂O system, Cr/H₂O system and Ni/H₂O system for supercritical water. The boundary condition between solids and ionic species was put at 10⁻⁶ mol/kg. Judging from the diagrams above 500°C and 25 MPa, there is the possibility to reduce the value of pH below 11. The corrosion behaviours for the reactor core component materials will be affected by supercritical pressure water with the high intensity radiation field. A typical structure and composition profile for an oxide grown on an austenitic stainless steel can be seen in the SEM image and EDS profiles of Fig. 7. The cross-sectional EDS observation result of 1520Ti is shown in Fig. 7 after 1000 h corrosion with the large amount of corrosion.

Fig. 7: Cross-section SEM image and EDS profiles exposed to 600°C SCW for 1520Ti. The concentration of Cr decreased 50 µm from the surface of the specimen in the condition of 1520Ti at 600°C, 1000 h in supercritical water.

Additional information on oxide structure in austenitic stainless steels can be seen in Table 2. The gradient of Cr concentration in the matrix was not observed for 1520S. The cross-sectional analysis by SEM-EDS observation at 600°C 1000 h (SEI: ×400) for 1520Ti. The intensity of Cr in the range of 50µm from its surface decreased. The oxide layer of 1520Ti at 600°C consists of magnetite though the
bulk of the specimen that was in the iron-chromium-nickel base austenitic stainless steel. The oxide structures of both 1520S and 1520Ti at 400 °C and 500 °C were similar. The structure for 1520Ti corroded at 600 °C was composed of only magnetite. The difference between 1520S and 1520Ti austenitic stainless steels was the stability of the oxide layer at 600 °C. The 1520S austenitic stainless steels had the higher bulk concentrations of chromium and manganese. The Cr concentration in the range of 50μm from the surface had a tendency to be reduced from the bulk to the surface, as demonstrated in the view images exposed to 600 °C in supercritical water as shown in Fig. 7. The oxide/layer weights were obtained from the weight change before and after the removing scale processing. Each result shows that the tendency of corrosion at 600 °C differs from that those of 400 °C and 500 °C. The result for weight of scale W_S was shown in Fig. 5 as the same tendency as weight gain W_G and weight loss W_S were observed. After exposure for 1000h, the 1520S and 1520Ti samples had been caused to be corroded and exhibited no small cracks and spallation within error range. Judging from SEM-EDS observation, the specimens were covered with about 10 μm oxide layer after exposed at 600 °C, 1000h with 1520Ti and 1520S. It turns out that the surface of 1520Ti exposed at 600 °C was covered with grown-up grains by SEM-EDS cross sectional observation. The surface was covered by not Cr oxide but Fe_3O_4 magnetite phase by the result of XRD. However, the test materials used in this experiment were the solved processing materials that can be improved to satisfy the required characteristics with adjustment for the system by heat treatment, the concentration of elements, cold works and so on.

4. Conclusion
As for general corrosion, 1520S may have a more possibility than 1520Ti to adopt a supercritical water reactor core fuel cladding. There are substantial differences between 500 °C and 600 °C for the weight gain, weight loss and weight of scale for both 1520S and 1520Ti. These materials showed good corrosion resistance to be used below 500 °C in supercritical water. The addition of Ti lets the surface increased corrosion above 600 °C. The XRD results indicated the substantial formation of magnetite for 1520Ti. The EDS analysis showed the decrease of Cr content in the range of 50μm from the surface. This implies that the decrease of Cr content at surfaces causes the reduced corrosion-resistant characteristics. The surfaces of 1520S at 600 °C were not observed to elute Cr from them.

5. Acknowledgements
The Present study is the results of “Research and Development of the Super Fast Reactor” entrusted to the University of Tokyo by the Ministry of Education, Culture, Sports, Science and Technology and Japan (MEXT).

6. References
[1] Oka Y and Koshizuka S 2000 Proc. of SCR-2000 Conf. (Yokohama Japan 6-9 Nov 2000) (Tokyo: Japan Society for the Promotion of Science) ed Y Katsumura et al (Tokyo: University of Tokyo) p 101
[2] Koshizuka S and Oka Y 2000 Proc. of SCR-2000 Conf. (Yokohama Japan 6-9 Nov 2000) (Tokyo: Japan Society for the Promotion of Science) ed Y Katsumura et al (Tokyo: University of Tokyo) p 302
[3] Jaewoon Y, Ishiwatari Y and Oka Y 2006 Annuals of Nuclear Energy vol. 33, ed L E Weaver, M M R Williams et al (Amsterdam: Elsevier) pp 945-956
[4] Was G S, Ampornrat P, Gupta G, Teysserey S, West E A, Allen T R, Sridharan K, Tan L, Chen Y, Ren X and Pister C 2007 J. Nucl. Mater. 371 176-201
[5] Mitton D B, Kim H, Kim J K, Latanision R M, McKinley J, Teysserey S and Was G S 2003 Proc. of Int. Congress Advances in Nuclear Power Plants 2003 (Córdoba, Spain, 4-7 May 2003) (Sociedad Nuclear Española, Société Française d'Energie Nucléaire, American Nuclear
[6] Kaneda J, Kasahara S, Kuniya J, Kano F, Takahashi H and Matsui H 2007 Proc. of Int. Congress Advances in Nuclear Power Plants 2007 (Nice, France, 13-18 May) (French Nuclear Energy Society) ed G Servière, D Spurgeon et al (Paris: French Nuclear Energy Society) p 7500

[7] Katsumura Y, Kiuchi K, Domae M, Wada Y and Yotsuyanagi T 2003 Proc. of Int. Congress Advances in Nuclear Power Plants 2003 (Córdoba, Spain, 4-7 May 2003) (Sociedad Nuclear Española, Société Française d'Energie Nucléaire, American Nuclear Society, Korean Nuclear Society and Atomic Energy Society of Japan) ed S Anghaie and L Schreiber (Florida: Gainesville) p 1178

[8] Saito N, Tsuchiya Y, Kano F, Ookawa M, Kaneda J, Moriya K and Matsui H 2006 Proc. of Int. Congress Advances in Nuclear Power Plants 2006 (Reno, USA, 4-8 June 2006) (American Nuclear Society, Sociedad Nuclear Española, Société Française d'Energie Nucléaire, Korean Nuclear Society and Atomic Energy Society of Japan) ed F L Bowman et al (Washington DC: Nuclear Energy Institute) p 6137

[9] Kasahara S, Kuniya J, Moriya K, Saito N and Shiga S 2003 Proc. of Int. Congress Advances in Nuclear Power Plants 2003 (Córdoba, Spain, 4-7 May 2003) (Sociedad Nuclear Española, Société Française d'Energie Nucléaire, American Nuclear Society, Korean Nuclear Society and Atomic Energy Society of Japan) ed S Anghaie and L Schreiber (Florida: Gainesville) p 1132

[10] Tsuchiya Y, Kano F, Saito N, Shiga S, Kasahara S, Moriya K and Takahashi H 2003 Proc. of Int. Congress Advances in Nuclear Power Plants 2003 (Córdoba, Spain, 4-7 May 2003) (Sociedad Nuclear Española, Société Française d'Energie Nucléaire, American Nuclear Society, Korean Nuclear Society and Atomic Energy Society of Japan) ed S Anghaie and L Schreiber (Florida: Gainesville) p 1096