Accelerated Thermal Aging of High Nitrogen Austenitic Stainless Steel for Long-Term Thermal Degradation Simulation: Microstructural and Mechanical Property Evaluation

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1. Introduction

High nitrogen austenitic stainless steel (ASS) is being actively investigated as a suitable material for structural applications in small modular reactors (SMRs) due to its excellent strength, ductility, and corrosion resistance [1]. However, exposure to high temperature during service can induce microstructural changes, potentially degrading its mechanical properties. During extended operation at typical SMR temperatures (285–300 °C), Cr-rich carbides ($M_{23}C_6$) and nitrides (Cr_2N) can precipitate at grain boundaries, which is known as sensitization [2]. This phenomenon can potentially reduce the corrosion resistance of High nitrogen ASS. Most of the intermetallic phases are detrimental to the mechanical and corrosion properties of the ASS [3,4]. Understanding the thermal aging effect of High nitrogen austenitic stainless steel is essential to ensure its long-term performance and reliability in SMR environments, where material stability and predictability are critical for safety and efficiency.

This study investigates the effects of thermal aging on the microstructural evolution and mechanical properties of High nitrogen ASS with a nitrogen content of approximately 0.4 wt%. Specimens will be aged at 400°C for up to 5,000h, and this paper presents initial analysis results for up to 1,000 h. Microstructural evolutions are systematically investigated by using optical microscope (OM), scanning electron microscope (SEM), and transmission electron microscope (TEM). Additionally, mechanical properties, including hardness and tensile properties, are evaluated.

2. Methods

2.1 Material and heat treatment

The materials used in this study were High nitrogen ASS blocks, provided by Korea Atomic Energy Research Institute (KAERI). The chemical composition of the blocks used in this study is presented in Table 1. The material was solution-annealed at 1090 ◦C for 0.5 h followed by a water quench. The water temperature was a maximum of 38°C before quenching and a maximum of 49°C after quenching. Thermal aging treatment was performed in the electric pit-type heating furnace at 400 ◦C for 1,000 h. respectively, followed by air cooling. Figure 2 shows the sample arrangement in the furnace.

Table I: Chemical composition of High nitrogen ASS [wt.%]

Fe	Cr	Ni	Mn	Mo	Si
Bal	21.51	12.04	4.94	2.03	0.39
N	Nb	V	P	C	S
0.338	0.18	0.12	0.027	0.032	<0.0005

Fig. 1. High nitrogen ASS block.

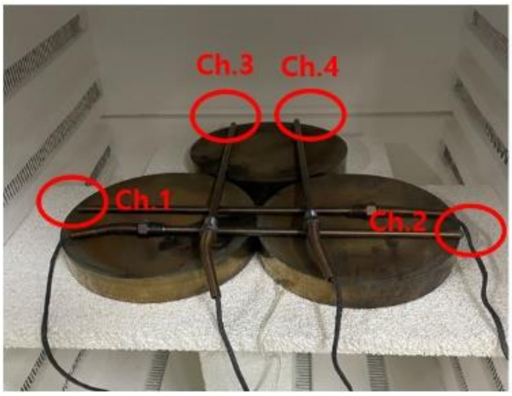

Fig. 2. The sample arrangement and TC placement in the furnace.

2.2 Microstructural characterization

The microstructures of the as-received and aged samples were examined under an optical microscope and scanning electron microscope (SEM) after polishing with diamond paste to 1 um finish and etching. Electrolytic etching of the samples was done in 10% oxalic acid solution at 5V. The chemical composition of the individual phases of austenite was measured using a scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectrometer (EDS).

As-recrived and aged samples were also examined using transmission electron microscopy (TEM) to study the phase transformations after thermal aging.

3. Results and Discussion

3.1 Thermal aging conditions

To simulate the condition of structures in long-operated nuclear power plants within a reasonable time, the aging process in the test material must be accelerated. However, for this approach to be valid, Secondary phases that do not form in the actual operating environment should not appear at accelerated aging temperatures. During extended operation at typical SMR temperatures (285–300 °C), Cr-rich carbides ($M_{23}C_6$) and nitrides (Cr_2N) can precipitate at grain boundaries, which is known as sensitization [3,4]. This phenomenon can potentially reduce the corrosion resistance of High nitrogen ASS. Calculations using a thermodynamic simulation program [5] indicate that the phase fraction changes drastically at temperatures higher than 400°C, as shown in Figure 3 and Table 2. At this temperature, the same types of precipitates (Cr-rich $M_{23}C_6$ and Cr_2N) form more rapidly, effectively reducing experimental time. Y. Fan et al. [6] reported that no carbide precipitations or secondary phases are observed in 316LN ASS after thermal aging at 400 ◦C for up to 10,000h. Therefore, the aging temperatures was selected to be 400 ◦C.

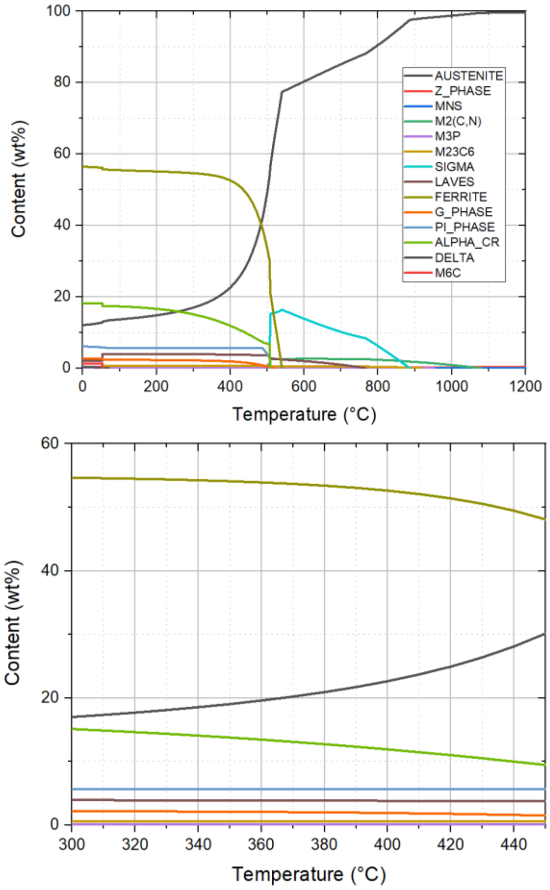

Fig. 3. Phase diagram of High nitrogen ASS using a thermodynamic simulation program [5],
(top) Overall phase diagram with temperature.
(bottom) Phase diagram in the range of 300°C to 450°C.

The degradation behavior of materials under long-term thermal aging is inherently influenced by temperature and time. Therefore, it can be understood based on the Arrhenius equation, which describes the relationship between these two factors. The Arrhenius model is one of the most widely used methods for simulating thermal degradation and has been recognized by the NRC as an appropriate approach for accelerated aging simulations [2-7].

To determine the temperature and time required for simulating long-term thermal aging, the activation energy for thermal embrittlement of the material is essential. Although no prior studies have been conducted on High nitrogen ASS, a model has been proposed to predict the activation energy for thermal embrittlement based on composition using data from thermally aged CASS in the 300–400°C range, as shown in Table 3 [8-10]. Lee et al. [11] found that Mager’s model was developed using GF data, making it well-fitted to that dataset. However, it underpredicts the results for the ANL/FRA dataset obtained later. Chung’s model can be useful for identifying trends in newly evaluated CASS materials, but it may not be suitable when high prediction accuracy is required. Chopra’s model tends to overpredict, with some CF-3 and CF-3M materials showing excessively high predicted values.

Mager’s model was calculated without considering the contribution of Mn, making it insufficient to fully reflect the compositional characteristics of High nitrogen ASS, potentially leading to overestimated values. In contrast, Chopra’s model, with Cr and Ni contents similar to those of High nitrogen ASS, provides predictions that closely align with the chemical characteristics of High nitrogen ASS, except for differences in Mn content. Therefore, considering the compositional characteristics of High nitrogen ASS, this study applies the activation energy for thermal embrittlement calculated using Chopra’s model, which is 165.6 kJ/mol. The required heat treatment time was calculated assuming long-term thermal aging for 80 years at 300°C. When performing accelerated aging at 400°C, approximately 4,000 hours were determined to be necessary.

Table II: Phase fraction of High nitrogen ASS using a thermodynamic simulation program.

Temperature [°C]	Phase [wt%]									
	Ferrite	Austenite	Alpha Cr	G	Laves	Pi	Z	M23C6	M3P	MNS
300	54.67	17.01	15.12	2.22	3.94	5.67	0.58	0.62	0.16	0.001
400	52.64	22.65	11.92	1.92	3.84	5.66	0.58	0.62	0.17	0.001
450	48.10	30.16	9.47	1.49	3.76	5.65	0.58	0.62	0.17	0.001

Table III: Equations for predicting the activation energy for thermal embrittlement based on composition.

Model	Equation
Mager's Q model [8]	$Q_{CV} = -182.6 + 19.9Si + 11.08Cr + 14.4Mo$
Chung's Q model [9]	$Q_{CV}^{ANL} = 90.54 + 9.62Cr - 8.12Ni - 7.35Mo + 20.59Si - 123.0Mn + 317.7N$
	$Q_{CV}^{GF} = -66.65 + 6.90Cr - 5.44Ni - 8.08Mo + 17.15Si + 44.1Mn + 297.1N$
Chopra's Q model [10]	$Q_{CV}^{CF3/CF8} = 10[74.52 - 7.20\theta - 3.46Si - 1.78Cr + 148N - 61C]$
	$Q_{CV}^{CF8M} = 10[74.52 - 7.20\theta - 3.46Si - 1.78Cr - 4.35Mn + 23N]$

3.2 Heat treatment

Experiments had been conducted up to 1,000 h. During experiment, the temperature inside the furnace was measured and monitored. As below figure shows, test temperature had been uniformly maintained during the experiment.

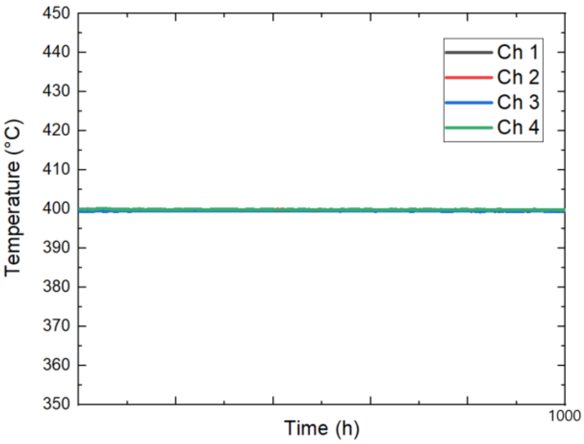

Fig. 4. Furnace operating temperature during the experiment.

3.3 Microstructure evolution after aging

Figure 5 and 6 presents the microstructure of the High nitrogen ASS. It exhibited a single austenitic phase with twins located inside the austenitic grains. The grain size of the High nitrogen ASS is approximately 21.0 µm using Image J program. Plenty of voids can be observed inside and at the grain boundaries in the High nitrogen ASS [12].

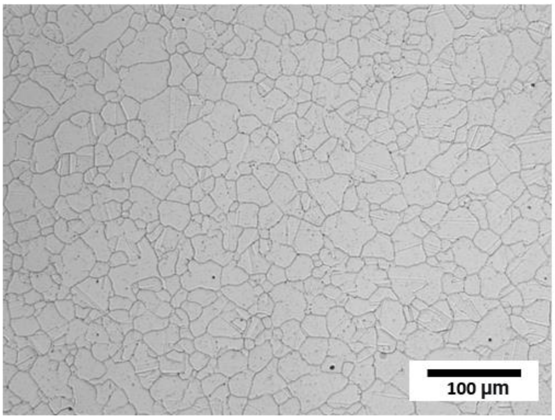

Fig. 5. Typical OM image of High nitrogen ASS.

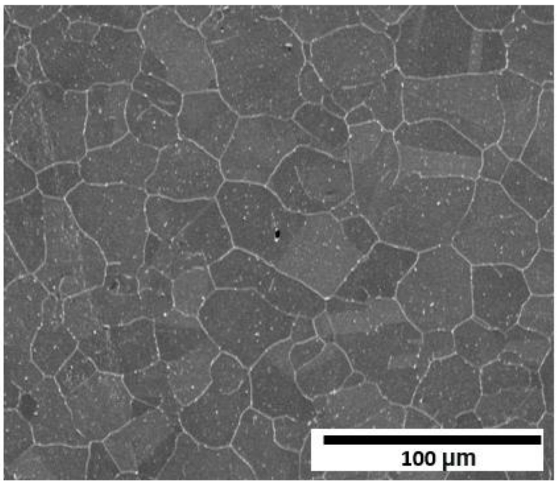

Fig. 6. Typical SEM image of High nitrogen ASS.

2.2 Effect of aging on microhardnes and tensile properties

The micro-hardness of the High nitrogen ASS after thermal aging is planned to measured. The microhardness in austenite phase is expected to remain unaffected after thermal aging treatment, and the same results have already been reported by other investigators [13-15].

3. Conclusions

Accelerated thermal aging was performed to simulate the condition of structures in long-operated nuclear power plants within a reasonable time. Secondary phases that do not form in the actual operating environment should not appear at accelerated aging temperatures in the High nitrogen ASS. This was verified through a thermodynamic simulation program, which confirmed that such phases do not form under the selected conditions.

In this study, the Arrhenius equation was applied to design an accelerated aging experiment, considering the inherent dependence of long-term thermal degradation on temperature and time. To accurately simulate thermal embrittlement behavior, the activation energy is a crucial parameter. Given the absence of prior studies on High nitrogen ASS, Chopra's model was selected to estimate the activation energy based on compositional similarities with High nitrogen ASS. Using this approach, the activation energy for thermal embrittlement was determined to be 165.6 kJ/mol.

Based on this activation energy, the required heat treatment time was calculated to simulate long-term thermal aging for 80 years at 300°C. When applying accelerated aging at 400°C, approximately 4,000 hours were determined to be necessary, ensuring a reasonable experimental timeframe while maintaining phase stability and degradation mechanisms consistent with actual operating conditions.

The effects of thermal aging on the microstructural evolution and mechanical properties of the High nitrogen ASS was studied after thermal aging at 400 ◦C for 0h and 1000 h. The microstructural evolutions will be evaluated using OM, EBSD, SEM, and TEM. Additionally, mechanical properties, including hardness and tensile properties, will also be examined.

ACKNOWLEDGEMENT

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