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[Technical Paper]

The Corrosion Behavior of Cold-Rolled 304 Stainless Steel In Salt Spray Environments

염분분사 환경에서 냉연 304 스테인레스강의 부식거동

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Abstract

Saline corrosion is one of the major degradation mechanisms for stainless steel type 304 (SS304) dry storage cask during the spent fuel interim storage period. Slow strain rate test (SSRT) and neutral salt spray test (NSS) were performed at 85°C and 200°C with 0.5 wt% sodium chloride mist sprayed on the cold-rolled SS304 specimens of different degrees of reduction in this study. The weight changes of the NSS specimens tested at 85°C for 2000 hours differed greatly from those at 200°C. The weight loss of NSS specimens was not significant at 85°C but the weight gain decreased gradually with increasing the cold-rolled reduction. The yield strength (YS) and ultimate tensile stress (UTS) values obtained from the SSRT tests for lightly cold-rolled specimens in the salt spray environment at 85°C and 200°C are slightly lower than in air. But for those with 20% reductions, the specimen strengths were no longer changed by the saline corrosion. The preliminary results demonstrated that the quality and performance of cold-rolled SS304 is acceptable for fabrication of dry storage casks. However, more work on the corrosion behavior of cold-rolled stainless steel in the saline atmosphere is needed to better understand its long-term performance.

Key words : storage cask, spent fuel, saline corrosion, stainless steel, strength

요 약

염분분위기에서의 부식은 사용후핵연료의 중간저장 기간 동안 304 스테인레스 강재 건식저장용기의 주 열화기구들 중 하나다. 본 연구에서는 감소정도가 서로 다른 냉연 304 스테인레스 강 시편들에 0.5wt.%의 염화나트륨 연무를 분사시키면서 느린 변형속도시험(SSRT)과 중성염 분사시험(NSS)을 85℃와 200℃에서 수행하였다. 85℃에서 2000 시간 동안 시험한 NSS시편의 무게 변화는 200℃에서 시험한 시편의 무게 변화와 크게 달랐다. NSS 시편의 85℃에서 무게 감량은 미미하였지만, 냉연 감소율이 증가함에 따라서 무게 변화는 점진적으로 감소하였다. 85℃와 200℃에서 그리고 염분분사 환경에서 가볍게 냉연 가공된 시편의 SSRT 시험으로부터

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얻은 항복강도와 극한 인장응력의 값은 공기 중의 값보다 약간 낮았다. 그러나 염분 분위기에서 부식으로 인한 20% 감소 냉연시편의 강도는 더 이상 변화하지 않았다. 예비결과는 냉연 304 스테인레스 강의 질과 성능이 건식저장용기의 제작을 위한 조건에 맞는다는 것을 증명하였다. 그러나 냉연 스테인레스 강의 장기적인 성능을 더 잘 이해하기 위해서는 염분분위기에서 이 재질의 부식거동에 관한 더 많은 연구가 필요하다.

중심단어 : 저장용기, 사용후핵연료, 염분분위기부식, 스테인레스강, 강도

I. Introduction

Nuclear power plants have tentatively stored the used fuel, known as "spent fuel", in the spent fuel pool at the reactor site. For years, the need for alternative storage began to grow when pools began to fill up with the spent fuel at many nuclear plants. Due to the facile maintaining, easy administrating and convenient transportation outside the plants[1], the interim dry storage method is an option at present. Dry spent fuel storage in casks is considered to be safe and environmentally sound. Over the last 20 years, there have been no radiation releases which have affected the public, no radioactive contamination, and no known or suspected attempts to sabotage the storage cask. The interim storage has been proven safe and has been used by commercial utilities[2].

The material most commonly used for storage casks is stainless steel type 304 (SS304). But it is well known SS304 has a sensitization problem[3]. Sensitized grain boundaries may facilitate stress corrosion cracking (SCC) and present an easy crack propagation path[4]. The material factors affecting the SCC behavior include the cold plastic deformation and seam welding. The SCC susceptibility of SS304 has been proven to increase with the degree of cold work, especially above 40%[5~7]. Meanwhile other studies have shown that low levels of cold work seem to increase the resistance of chloride SCC up to an estimated maximum value of ~30% cold work[8~9].

After removing from the pool, the fuel rods are stored in an inert gas environment inside a large SS304 or SS316 storage cask. Stainless steel plates are first cold-worked by the forging and rolling process, and then are welded to manufacture a cask. When loaded with fuel bundles, the casks are filled with helium or nitrogen to help transfer the decay heat during the storage period. The inner temperature of the cask is estimated to be approximately to 200 °C and the outer temperature between 80 to 90 °C. These casks could be stored in arid zone such as deserts or sea shore near the plants. If near the shore, corrosion caused by the chloride ion and water vapor in the atmosphere becomes a critical issue for the life of the cask. In order to understand the reliability of the storage cask in the saline environment, the ability of the corrosion resistance and mechanical properties of cold-worked SS304 should be evaluated. The creviced bend beam (CBB) and compact tension (CT) tests on SS304 and SS316 have been done in solutions with highly corrosive concentrations[10~12], but the fracture behavior of the casks near the shore with lower salt concentrations has not been well studied. In this work, it was intended to investigate the fracture and corrosion behavior of cold-worked SS304 in a low-concentration salt spray environment by slow strain rate test (SSRT) and neutral salt spray test (NSS).

II. Materials and Experimental

The material employed in this investigation was 304 stainless steel plates with the chemical composition (wt %) of 18.1 Cr, 0.28 Mo, 0.022 C, 0.1 Co, 0.5 Si, 1.56 Mn, 0.0004 S, 0.48 Cu, 0.03 P and the balance Fe. The as-received material had been hot-rolled and annealed at 1100°C. Test specimens were cold-rolled to 5%, 10%, 20%, and 30% reductions in thickness.

Neutral salt spray test (NSS) was conducted as per ASTM standard G85. In order to simulate the real storage environment, the NaCl concentration for the test was lower than the requirements of ASTM G85 standard. The NSS specimens were machined to the dimensions of 60mm × 30mm × 2mm and grinded with emery paper to # 600 grit. Then, the specimens were put into the chamber equipped with spray of a 0.5wt% NaCl salt solution. Test temperatures were at 85 and 200°C. The test continued up to 2000 hrs and specimens were taken out of the corrosion chamber to measure the weight gain every 200 hrs.

The slow strain rate tensile tests (SSRT) were performed on the specimens (Fig.1) following ASTM E139. The test strain rate was at 1×10^{-6} per sec and test temperatures at 85 and 200°C. A box furnace was employed to control the temperature to an accuracy of ±2°C. The saline spray was applied during tensile testing. As the test terminated, the tensile properties in the saline environment and air were compared to understand the corrosion degradation behavior of stainless steel in the saline environment. The

Table 1. The YS and UTS lose (%) for SSRT specimens at 85 and 200°C.

	YS lose % 85°C	UTS lose % 85°C	YS lose % 200°C	YS lose % 200°C
As-received	12	1.5	0.4	0
5% cold-rolled	7.2	1.1	2.9	-0.2
10% cold-rolled	7.2	3.3	1.8	2.4
20% cold-rolled	-0.6	0.4	-1.2	-2.3
30% cold-rolled	-1.1	0.7	2.1	4.1

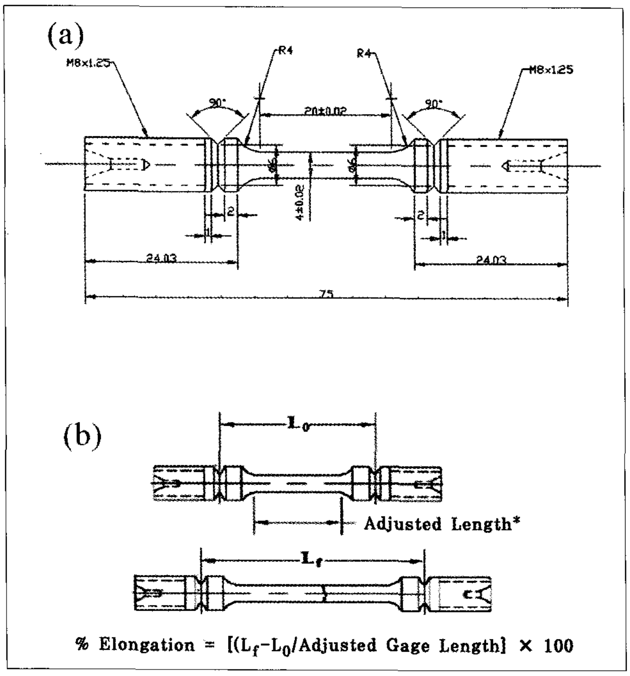

Fig. 1. The salt spray SSRT specimens: (a) dimensions of specimens and (b) the strain measurement method.

fracture appearance was examined by scanning electron microscopy (SEM).

III. Results and Discussion

1. NSS test

The weight variation of SS304 specimens after neutral salt spray tests at 85°C was plotted in Fig. 2(a). The weight of all the specimens increased slightly in the first 1200 hrs, decreased about 0.005g in the period of 1200 and 1400 hrs and then remained constant in the rest of the testing time. The as-received specimen had a weight increment of 0.01g relative to the cold-rolled ones. At 85°C, the cold-rolled specimens were not susceptible to saline corrosion, and the cold roll level showed no influence on saline corrosion resistance. The results obtained by NSS tests at 200°C, as shown in Fig.2(b), were different from those at 85°C. The weights of all specimens increased slowly in the first 400 hrs and then decreased. The cold-rolled specimens of higher cold-work levels had less weight variations than the as-received and lightly cold-rolled ones. As the results indicated, cold-worked specimens had better resistance to saline corrosion at 85°C and 200°C. Apparently, the degree

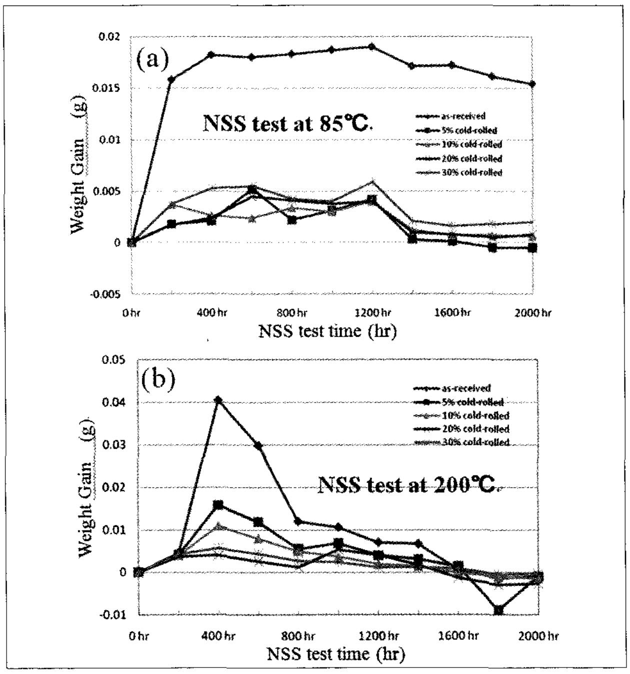

Fig. 2. The weight variations of SS304 specimens after NSS tests at (a) 85°C and (b) 200°C.

of cold-rolled reduction showed no effects on the saline corrosion behavior of SS304 at 85°C, but played an important role at 200°C.

2. SSRT Results

The results obtained by SSRT tests in air and saline environments at 85°C and 200°C were shown in Fig. 3(a) and (b), respectively. The yield strength (YS) and ultimate tensile strength (UTS) increased both at 85°C and 200°C as the cold-rolled deformation increased. As shown in Fig. 3(a), the YS and UTS for 5 % and 10% cold-rolled SS304 tested in the saline environment were lower than those in the air, including the as-received one. However, the YS and UTS obtained for 20% and 30% cold-rolled specimens tested in the air were lower than those in the saline environment. The SSRT results at 200°C are shown in Fig. 3(b). In the saline environment, it showed a general trend to increase the YS and UTS of SS304 with increasing the cold-rolled reduction level except those for 20% reduction specimen. The YS and UTS of 30% cold-rolled SS304 specimen even had a 4% UTS loss in the saline environment, but the as-received specimen had almost no variation in the results of the YS and UTS in air and the saline environments at 200°C. The SSRT results indicated that the 20% cold-rolled reduction could be the cold work level for SS304 to resist the saline corrosion both at 85 and 200°C. Furthermore, the lower cold-work level like 5% and 10% were not beneficial to the corrosion resistance of SS304 in the saline environment.

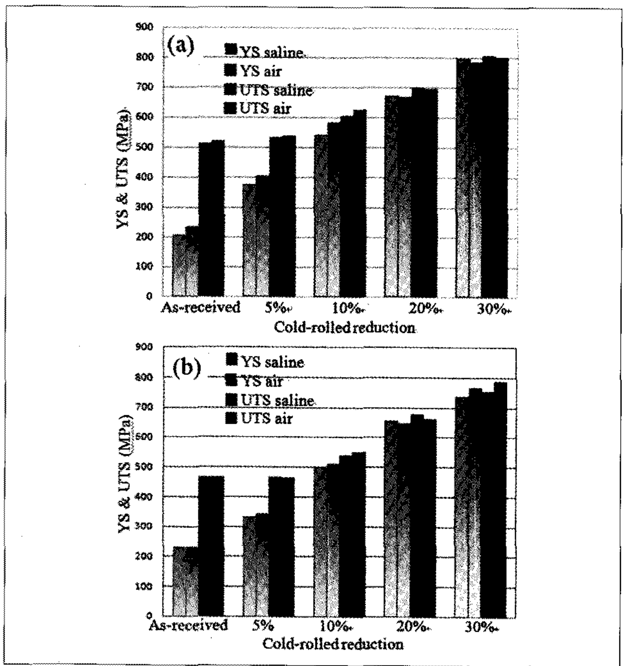

Fig. 3. Tensile properties of cold-rolled SS304 specimens obtained by SSRT tests in air and saline environment at (a) 85°C and (b) 200°C.

3. Fractographic Analysis

The fracture surfaces of the SSRT specimens were examined using scanning electron microscope (SEM). Two distinct areas, the SSRT zone and mechanical failure zone, were observed. A concentric fracture profile was revealed on the SEM fractograph of 5% cold-rolled specimen in air at a low magnification (Fig.4). The mechanical failure zone was surrounded by the SSRT zone. The SSRT zone and mechanical failure zone have distinctive fracture features, as revealed at a higher magnification in Fig.5. Dimples in the SSRT zone were smaller than those observed in the mechanical zone and had a specific orientation. During the slow strain rate tensile test, smaller and oriented dimples in the SSRT zone were initiated in the initial fracture stage, and big dimples in the mechanical failure zone during the final fracture stage. Ductile fracture features, as shown Fig.5(b), are evidence of the final failure due to mechanical overloading.

The SS304 specimens which were corroded by salt spray were revealed to have different fracture features.

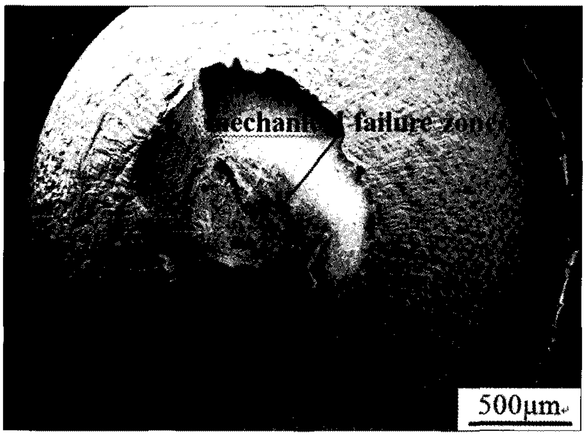

Fig. 4. Concentric fracture profile of 5% cold-rolled SS304 tension specimen tested in air. The SSRT zone and mechanical failure zone were the two distinctive fracture zones.

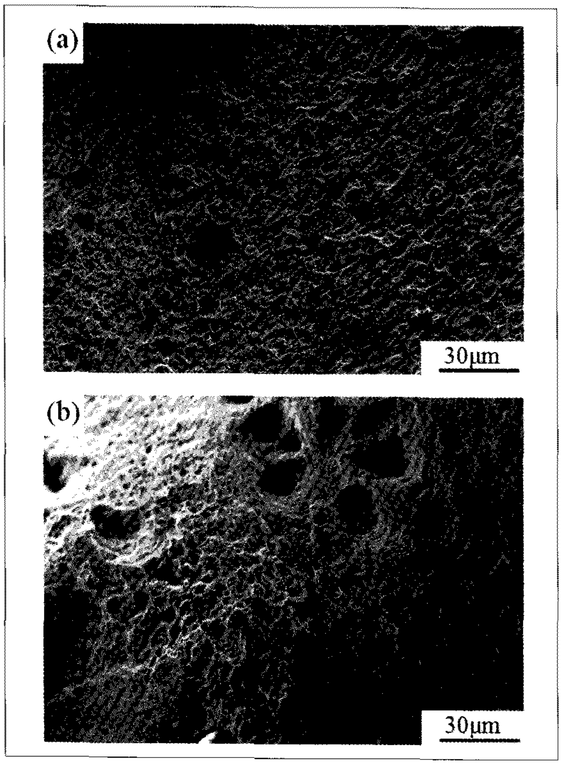

Fig. 5. The SEM fractographs of : (a) SSRT zone and (b) mechanical failure zone had distinctive fracture features.

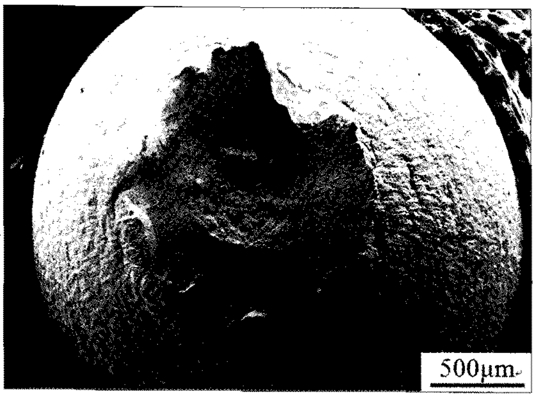

Fig. 6. The irregular fracture profile of 10% cold-rolled SS304 specimen tested in the saline environment at 85°C.

The fracture profile of the cold-rolled SS304 specimens of 10% reduction by SSRT tested (Fig. 6) in the saline environment at 85°C was irregular. Corrosion-initiated cracks prompted inhomogeneous plastic deformation during tensile testing. The observations that YSs and UTSs obtained from the tests in the saline environment were lower than those in air could be accounted for by the inhomogeneous plastic deformation. On the contrary, the tensile specimens with salt-spray corrosion resistance showed no local inhomogeneous deformation both in the saline environment and air. For instance, 20% cold-rolled specimens had the same circular fracture profile in the saline environment as in air (Fig.7). It was noted that the salt spray effecting area, Fig.8, displayed typical brittle fractures. These brittle zones were usually observed on the crack initiation areas of the local periphery on the fracture surface of the specimens which had lower YS and UTS in the saline environment than in air. The trans-granular split including secondary cracks, as indicated by arrow in Fig.8, on the salt spray effecting area are the typical fracture features of SCC which proved to be the SS304 deterioration mechanism in the saline environment. In other words, salt spray prompted corrosion cracking and resulted in the degradation. However, the corrosion resistance of SS304 with a particular cold-work level in the saline environments will be improved.

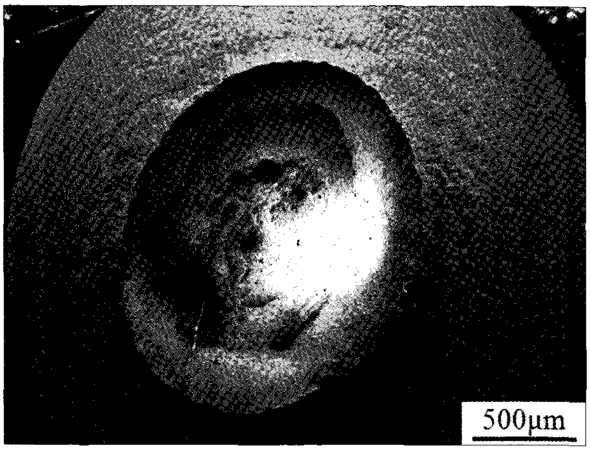

Fig. 7. The 20% cold-rolled specimens tested in the saline environment showed no local inhomogeneous deformation.

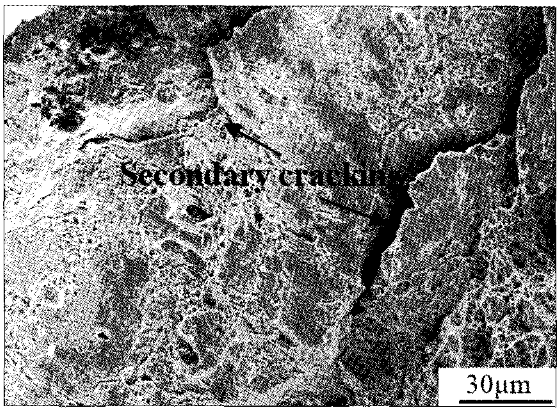

Fig. 8. A typical brittle fracture in the SSRT zone of the specimens tested in saline environment.

IV. Conclusions

1. The weight gain of SS304 NSS specimens in the salt spray environment was significantly decreased by prior cold work. Furthermore, the corrosion resistance of SS304 will be especially improved at 200°C saline environments by increasing the cold-rolled reduction level.

2. SSRT data revealed that the cold-rolled specimens of larger reductions showed better tensile properties at 85°C, but that the cold-rolled one of 5% reduction and annealed specimen (as-received) showed better performance at 200°C.

3. The 20% cold-rolled reduction specimens had best salt-corrosion resistance by the SSRT tests both at 85°C and 200°C SS304 which had been cold-worked to a specific level had shown better tensile properties in the saline environments, but it was difficult to elucidate the mechanism for this phenomenon.

4. The SSRT fracture morphology exhibited two distinct areas; an SSRT zone and a mechanical failure zone. The trans-granular split feature and secondary cracks were observed in the crack initialed areas of the SSRT zone of specimens whose YS and UTS were degraded by salt spray. This typical SCC features proved to be the deterioration mechanism for SS304 in the saline environments.

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