

# Effect of Thermal History on Pitting Corrosion of High Nitrogen and Low Molybdenum Stainless Steels

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Chromium, molybdenum, and nitrogen are very important alloying elements in stainless steels and its effect was approved in pitting resistance equivalent (PRE) equations and many experimental results. However, Cr can improve the corrosion resistance, but facilitate the formation of sigma phase. Also, Mo has the same effect in stainless steels. If Cr and Mo are added at high amount to increase the corrosion resistance of stainless steel, corrosion resistance in annealed alloys can be improved, but in case of welding or aging heat treatment, its resistance will be drastically decreased. In this work, increasing Cr and N contents but decreasing Mo than the commercial alloys made the experimental alloys. Typical alloys are 25Cr-4.5Mo-0.43N alloy, 27Cr-4.7Mo-0.4N alloy, 27Cr-5.3Mo-0.25N alloy, 32Cr-2.6Mo-0.36N alloy. After annealing and aging heat treatment, microstructures, anodic polarization test, and pitting corrosion test were performed. Annealed alloys showed 100°C of CPT and aged alloys showed the different tendency depending upon Cr and Mo contents(SFI)

**Keywords** : *austenitic stainless steel, duplex stainless steel, thermal history, corrosion resistance, chromium, molybdenum, and nitrogen*

## 1. Introduction

It is well known that stainless steels are prone to localized corrosion when those are subjected to aging heat treatment. Aging treatment facilitates the formation of sigma and kai phases, which are Cr and Mo rich phase. By the enrichment of Cr and Mo, Cr and Mo deleted zone can be formed near those phases and then this area acts as the initiation site for localized corrosion.<sup>1)</sup>

In duplex stainless steels that are composed of austenite and ferrite, generally, corrosion resistance of austenite is increased even though Cr and Mo contents are lower than those of ferrite, because nitrogen is almost dissolved in austenite.<sup>2,3)</sup> Especially, ferrite/austenite ratio is very important in pitting corrosion resistance and the ratio can be controlled by Ni and nitrogen contents. Aging treatment to duplex stainless steels also forms sigma and kai phases, and ferrite first decomposed to austenite (II) and then sigma and kai phases.<sup>1,2,4,5)</sup>

To evaluate the feasibility for sigma phase formation, sigma formation index, SFI [%Cr + 3.3(%Mo + 0.5%W)], occasionally, is used. This group showed the critical value of SFI in duplex stainless steel is under 35~36,<sup>6)</sup> but in

case of austenitic stainless, its value is not clear.

In this work, stainless steels containing high Cr, N and low Mo are melted and pitting resistance, polarization behavior, and microstructures about these castings are evaluated by annealing and aging heat treatment.

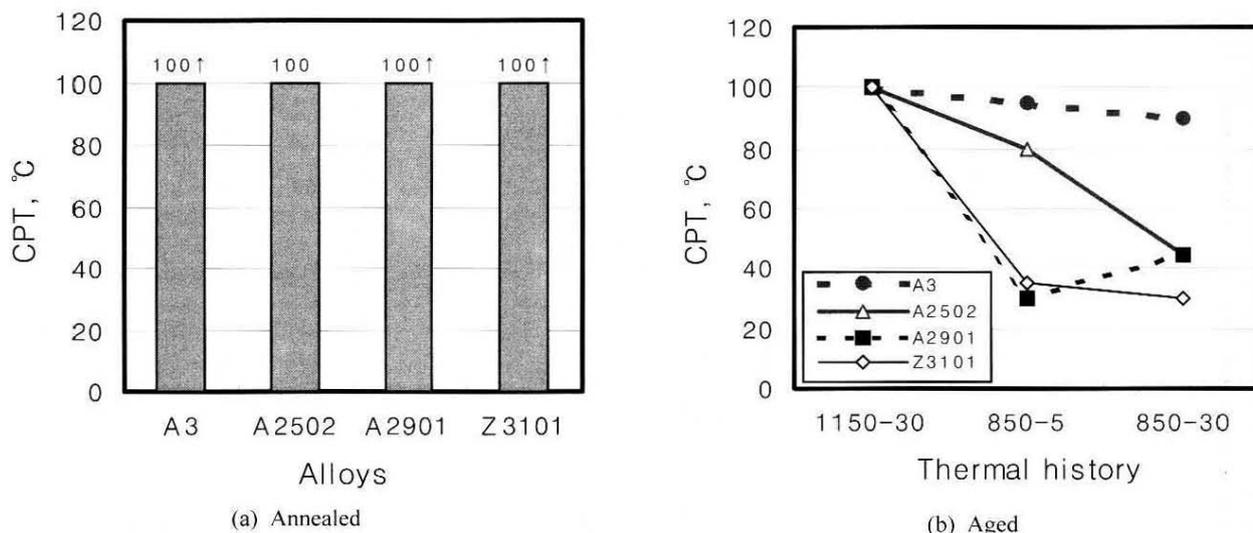
## 2. Experimental

Alloy A3 is melted by VIM and the others (Alloys A2502, A2901, and Z3101) are by AIM, and its chemical composition is shown in Table 1. These castings are annealed for 30 min. at 1150°C and then are aged for 5 min. or 30 min. at 850°C.

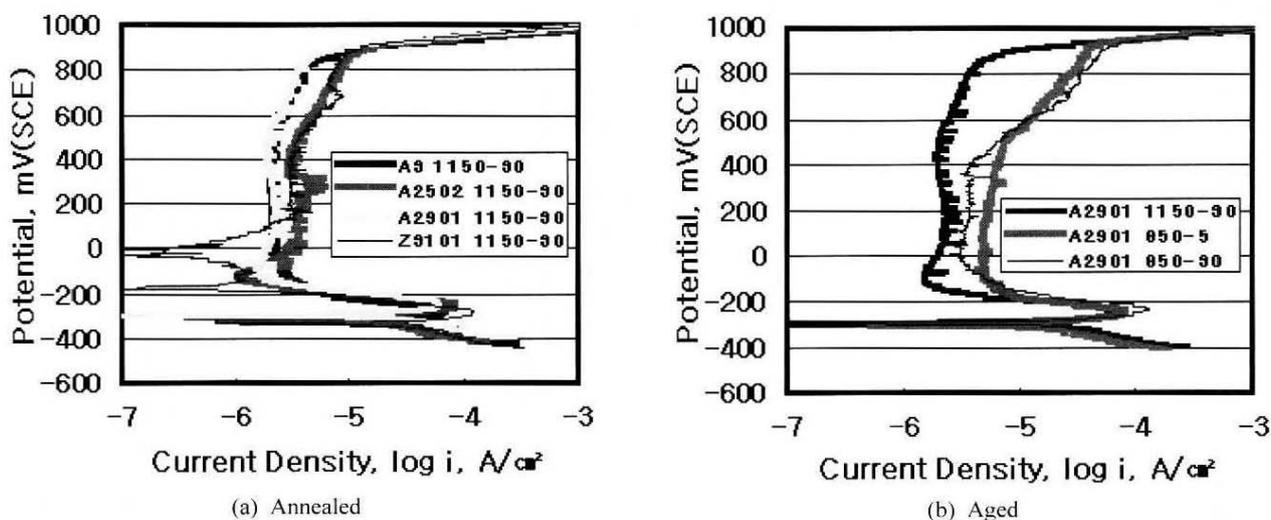
Microstructure is observed using optical microscope, SEM-EDS, XRD(2 theta 40~95°, 4°/min, or 40~55°, 1°/min). Rockwell hardness test on surface and micro-Vickers hardness test on austenite and ferrite phase are performed. Pitting corrosion resistance is evaluated 6% FeCl<sub>3</sub> by ASTM G48.<sup>7)</sup> Anodic polarization test is done in 50°C deaerated 0.5N HCl + 1N NaCl solution.

**Table 1. Chemical composition of the experimental alloys (wt%)**

Alloys	Cr	Mo	W	Si	Ni	Mn	C	N	P	S	Cr/Ni	PRE	SFI
A3	25.10	4.52	-	0.44	17.48	0.47	0.298	0.428	0.009	0.003	1.12	52.9	40.02
A2502	26.88	4.70	-	0.86	18.76	0.88	0.027	0.430	0.018	0.006	1.16	55.3	42.39
A2901	27.30	5.30	1.59	0.91	29.92	0.84	0.060	0.250	0.0028	0.007	0.99	54.9	47.41
Z3101	32.10	2.60	-	0.98	23.00	3.30	0.060	0.360	-	-	1.07	51.5	40.68



**Fig. 1.** Critical pitting temperature of annealed and aged alloys in 6% FeCl<sub>3</sub> by ASTM G48



**Fig. 2.** Anodic polarization behavior in 50°C deaerated 0.5N HCl + 1N NaCl solution

### 3. Results and discussion

Fig. 1 shows the CPT (Critical Pitting Temperature,

which accumulated weight loss is over 5 mg at each testing temperature) in 6% FeCl<sub>3</sub>. As shown in Fig. 1a, annealed alloys represent the CPT and over 100°C (If the testing

temperature becomes over 85°C, ferric chloride solution may be breakdown, but the test was continued to boiling point). Pitting corrosion resistance of the experimental alloys is higher than that of 6Mo grade super stainless steel and this is due to high PRE value of the alloys.<sup>8)</sup>

However, as shown in Fig. 1b, aging treatment makes the alloys to be sensitive to pitting corrosion. Among the alloys, Alloy A3 shows high pitting resistance regardless of aging treatment, but the CPT of Alloy A2502 gradually is decreased and the CPT of Alloys A2901 and Z3101 are drastically lowered.

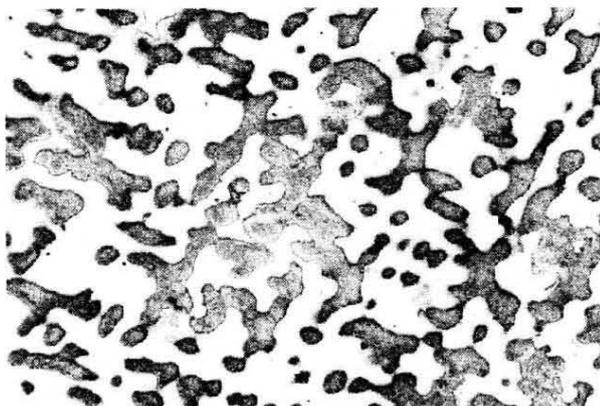
Fig. 2 shows the anodic polarization behavior of (a) annealed and (b) aged alloys in 50°C deaerated 0.5N HCl + 1N NaCl solution. Annealed alloys form the excellent passivity, but in case of aged alloy, the passive current density is increased and the transpassive behavior is shown over +400 mV(SCE).

High PRE's stainless steels generally show the better

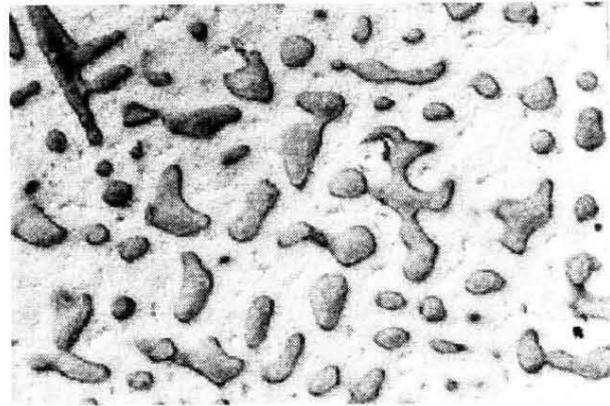
pitting resistance. PRE value of Alloys A3, A2502, A2901 and Z3101 is 52.9, 55.3, 54.9, and 51.5 respectively, and in case of annealed condition, all alloys show the similar resistance because of high PRE values. However, in case of aged condition, its resistance was dependent on alloy composition.

Fig. 3 shows the optical microstructures of annealed alloys. As shown in Fig., Alloys A3, A2502, and A2901 reveal the typical dendritic structure but Alloy Z3101 shows different microstructure. The second phase in Alloy Z3101 was revealed to be ferrite by EDS analysis. Ferrite content can be controlled by  $Cr_{eq}/Ni_{eq}$  ratio of alloys.<sup>1),9)</sup>

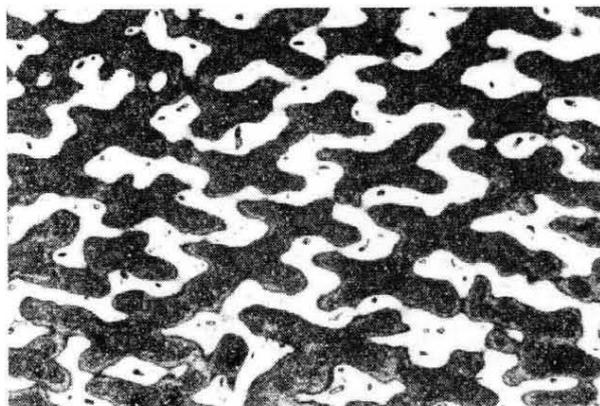
However, the ratios of the alloys are in the range of 0.99 ~ 1.16. Even though its ratio is similar to each other, different microstructure was obtained. This behavior seems to be related to Cr content of alloys. Alloy Z3101 has the ratio of 1.07 and the highest Cr content (32.1%) among the alloys. Therefore, it can be assumed that the relation



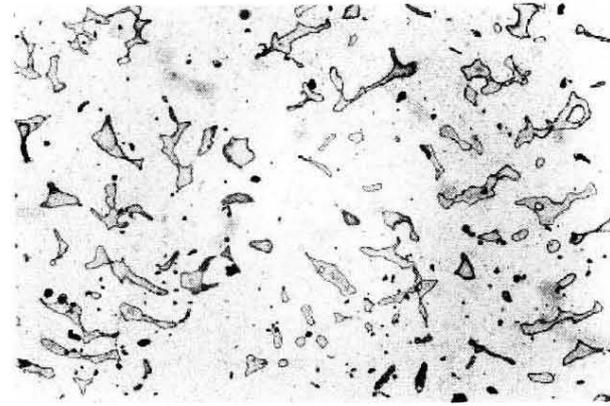
A3 1150-30( $\times 100$ )



A2502 1150-30( $\times 100$ )

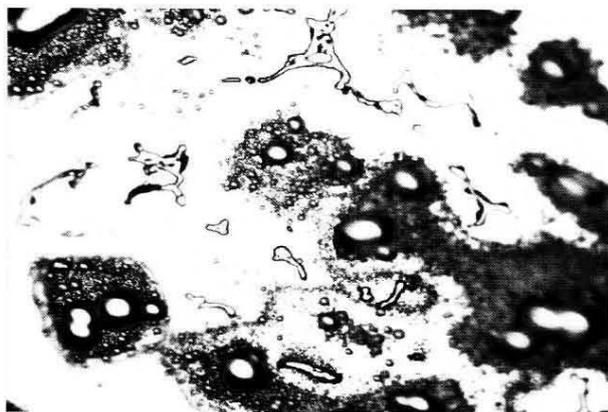


A2901 1150-30( $\times 100$ )



Z3101 1150-30( $\times 100$ )

Fig. 3. Optical microstructures of annealed alloys



(a) A3 1150-30 / 850-30( $\times 500$ )



(b) A2502 1150-30 / 850-30( $\times 500$ )



(c) A2901 1150-30 / 850-30( $\times 500$ )



(d) Z3101 1150-30 / 850-30( $\times 500$ )

**Fig. 4.** Effect of aging treatment on microstructural change

between ferrite content and  $Cr_{eq}/Ni_{eq}$  ratio may be non-linear.

Also, it should be noted that the small phase between dendrite is the primary delta ferrite in Alloys A3, A2502, and A2901, and this delta ferrite is very small amount and is easily destructed by mechanical process as like hot rolling. This delta ferrite didn't affect corrosion resistance in annealed condition.

Fig. 4 shows the optical microstructures of aged alloys. As shown in Fig., delta ferrite of Alloy A3 was not almost changed, and the ferrite of Alloys A2502 and Z3101 was decomposed, but Alloy A2901 showed the different grained structure. These structural changes may explain the deterioration of corrosion resistance by aging treatment.

Hardness of alloys by heat treatment was measured as shown in Fig. 5. Fig. 5a is surface Rockwell hardness (B scale) of annealed alloys. Fully austenitic stainless steels (A3, A2502, A2901) shows similar hardness regardless of

chemical composition, but Alloy Z3101 reveals relatively high hardness and this seems to be ferrite content in annealed structure.

Moreover, as shown in Fig. 5b, hardness of ferrite area is largely increased but that of austenite area still remains constant even aging time. Increased hardness of ferrite area in Z3101 means the formation of hard phase.

Fig. 6 represents the microstructural difference between delta ferrite and ferrite. Table 2 shows the EDS results on each point. In case of annealed austenitic steel, A2502 (Fig. 6a), delta ferrite is composed of 2~3 phases as like austenite, ferrite (and sigma). By aging treatment (Fig. 6b), the microstructure and composition were almost same.

However, as shown in Fig. 6c, ferrite phase in annealed Z3101 shows smooth and one phase. Aging treatment did affect the microstructure decomposition as like austenite (II) and sigma. This decomposition was approved in XRD analysis in Fig. 7.

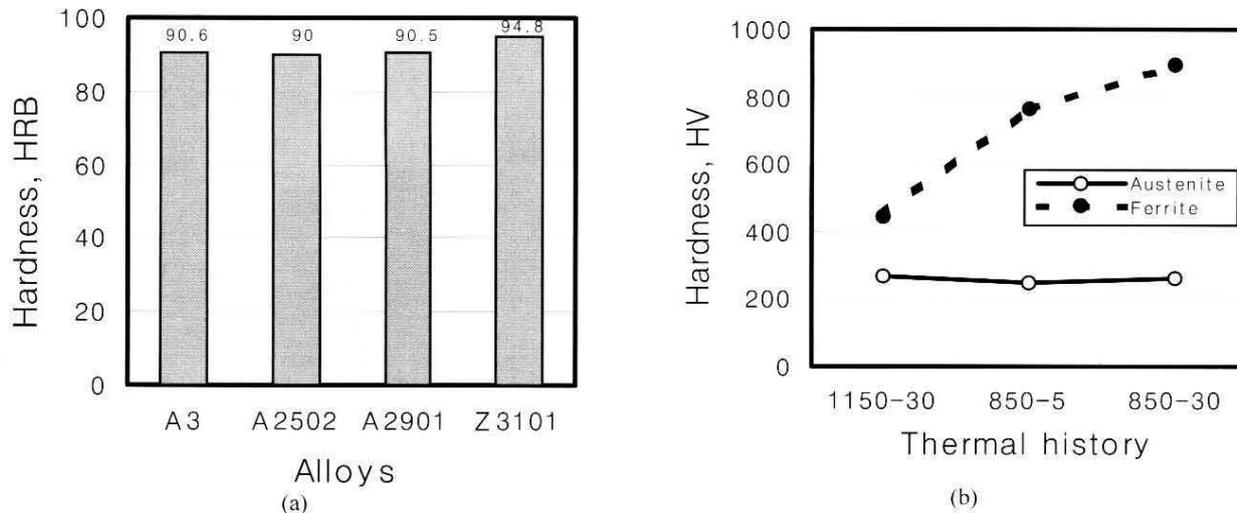


Fig. 5. (a) Rockwell hardness of annealed alloys and (b) Micro Vickers hardness of Z3101

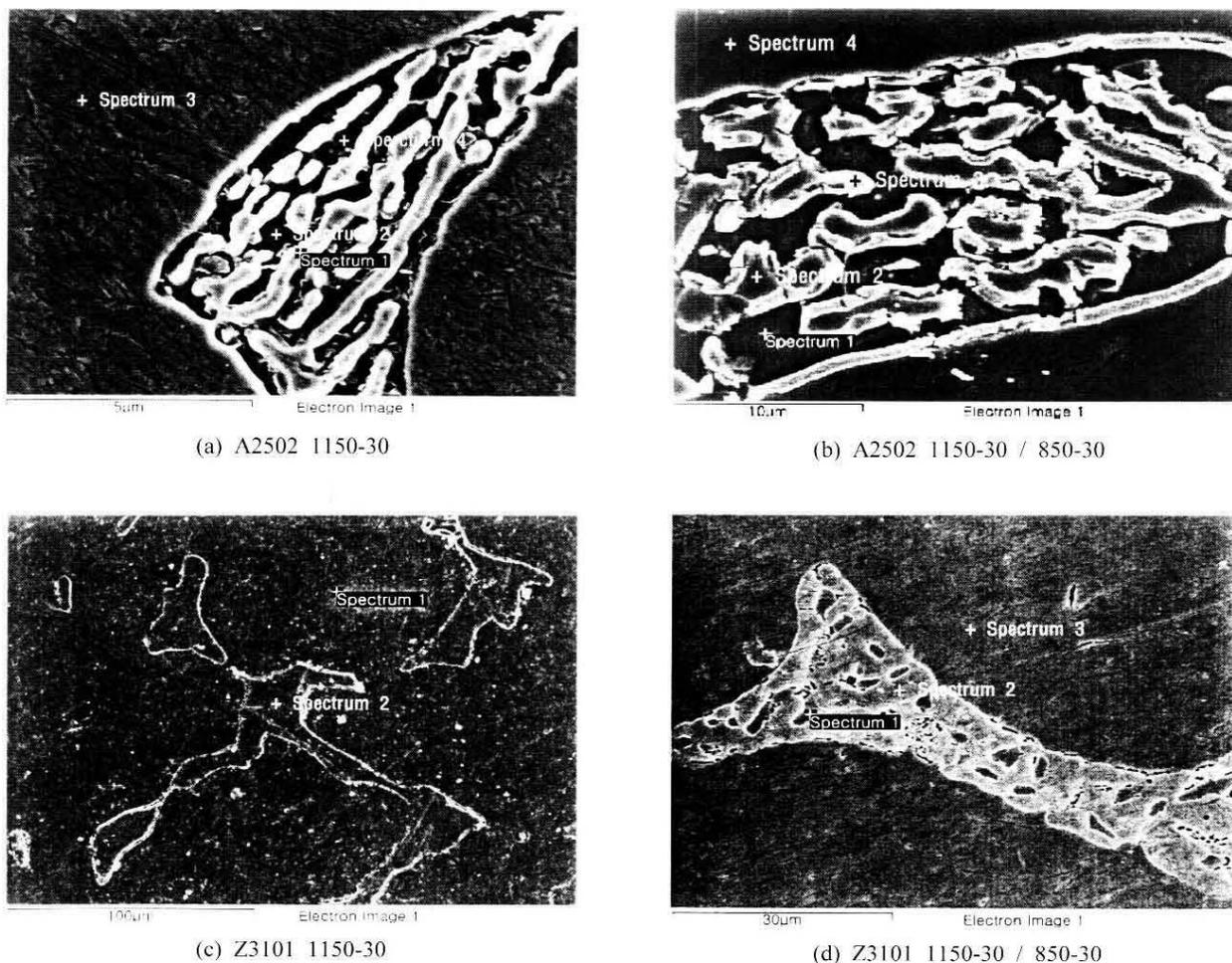
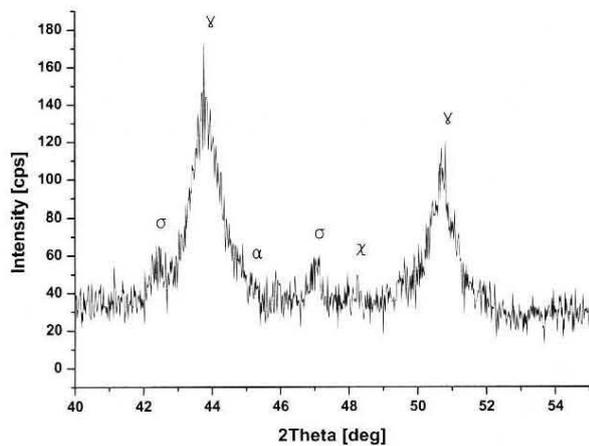


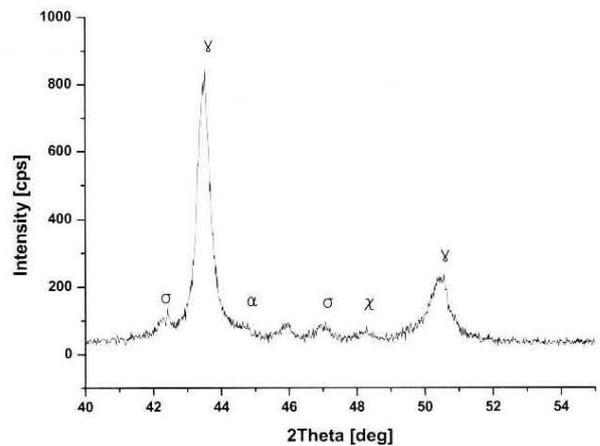
Fig. 6. SEM micrographs; (a) and (c) annealed condition, (b) and (d) aged

**Table 2. EDS result of Annealed and aged alloys (wt%)**

Specimen	Area	Si	Cr	Fe	Ni	Mo	Mn
(a) A2502 1150-30	Spectrum1( $\gamma$ )	1.32	28.37	45.39	20.03	4.90	-
	Spectrum2( $\alpha$ )	0.51	38.60	43.60	11.88	5.41	-
	Spectrum3( $\gamma$ )	1.01	28.02	46.00	20.27	4.69	-
	Spectrum4( $\sigma$ )	1.65	34.33	39.59	11.54	12.9	-
(b) A2502 1150-30 / 850-30	Spectrum1( $\sigma$ )	1.59	32.11	41.25	13.62	11.4	-
	Spectrum2( $\gamma$ )	1.17	28.80	46.20	19.23	4.60	-
	Spectrum3( $\alpha$ )	1.65	28.73	45.90	14.13	9.59	-
	Spectrum4( $\gamma$ )	1.03	28.25	46.12	19.78	4.82	-
(c) Z3101 1150-30	Spectrum1( $\gamma$ )	1.22	32.51	37.22	22.95	2.19	3.92
	Spectrum2( $\alpha$ )	1.31	38.42	37.38	15.49	3.77	3.63
(d) Z3101 1150-30 / 850-30	Spectrum1( $\gamma$ 2)	1.56	33.62	35.77	23.31	2.34	3.40
	Spectrum2( $\sigma$ )	2.14	40.80	33.67	14.29	6.11	2.98
	Spectrum3( $\gamma$ )	1.40	33.44	36.79	22.94	2.34	3.09

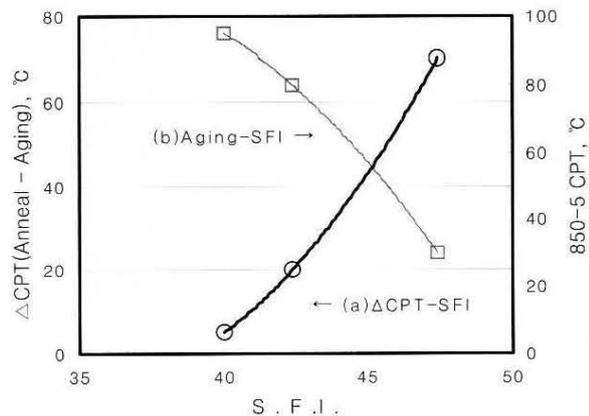


(a) A2502 1150-30 / 850-30



(b) Z3101 1150-30 / 850-30

**Fig. 7.** Identification of sigma formation by XRD analysis



**Fig. 8.** Effect of SFI on  $\Delta$ CPT and CPT of specimen aged at 850°C for 5 min.

Fig. 8 shows the effect of SFI on the degradation of pitting resistance of fully austenitic stainless steels. Increasing SFI value makes  $\Delta$ CPT between annealed and aged specimen more bigger and CPT of aged specimen sharply decreases with SFI increase. In case of duplex stainless steel, pitting resistance of aged specimen is drastically decreased when SFI is over 35–36.<sup>6)</sup> In case of austenitic stainless steels, critical SFI value seems to be over 40–43. However, more works should be needed.

#### 4. Conclusions

Stainless steels containing high Cr, N and low Mo are melted, and pitting resistance, polarization behavior, and microstructures about these castings are evaluated by

annealing and aging heat treatment.

High pitting corrosion resistant stainless steel showing CPT over 100°C in annealed condition is developed. However, aging heat treatment makes its resistance less, depending upon SFI values. In case of fully austenitic stainless steel, critical SFI value seems to be near 40~43.

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