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Effect of Cu Addition on the Properties of Duplex Stainless Steels

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The effect of addition of Cu on the localized corrosion performance of aged duplex stainless steel in chloride media has yet to be explained in a consistent manner, and there is some controversy in the literature regarding the composition of stainless steel and the experimental conditions (pH, temperature, chloride concentration, etc.) used. In this work, the effect of the addition of Cu on the microstructure, hardness, and corrosion resistance of duplex stainless steel in an acidic chloride or high concentration sulfuric acid solutions was investigated for annealed and aged alloys. The Cu addition of annealed duplex stainless steel strengthened the alloy and reduced the ferrite contents of the alloy, and it also increased the polarization behavior in chloride or sulfuric solutions, except for the case of a high potential in acidic chloride solution. However, the Cu addition of aged duplex stainless steel reduced the formation of harmful phases such as sigma and kai and increased the polarization behavior in acidic chloride or sulfuric solutions up to 0.8 wt% of the Cu content, after which it slightly decreased at 0.8 wt% Cu or more.

Keywords: *Duplex stainless steel, Copper, Sigma phase, Hardness, Corrosion*

1. Introduction

Duplex stainless steels with nearly equal fractions of ferrite and austenite phases are being increasingly used for various applications such as fuel gas desulphurization facilities in fossil power plants, desalination facilities, off-shore petroleum facilities, and chemical plants due to their high resistance to stress corrosion cracking, pitting corrosion, crevice corrosion, good weldability, excellent mechanical properties and relatively low cost due to the addition of low Ni relative to those of austenite stainless steels [1-5].

Super duplex stainless steels, such as UNS S32750, UNS S32760 and UNS S32550, are typically defined as duplex stainless steels with a pitting resistance equivalent (PRE = wt% Cr + (3.3 wt% Mo + 0.5 wt% W) + 16 wt% N) [6,7] of 40 to 45. Hyper duplex stainless steels such as UNS S32707 are defined as highly alloyed duplex stainless steels with a PRE exceeding 45 [6,8]. High corrosion resistance of super stainless steel was due to the synergistic effect of Mo and nitrogen [9].

It is well known that the addition of copper (Cu) to ferritic, austenitic or duplex stainless steels improves their resistance to general corrosion in sulfuric acid [10-14]. Some commercial duplex stainless steels include 0.5–1.0 wt% copper to improve corrosion resistance by reducing the corrosion rate in non-oxidizing environments, notably sulfuric acid [15-18]. The solubility of copper is relatively high in austenite (~4%) and low in ferrite (~0.2%) [19]. Aging after solution treatment causes significant hardening through the precipitation of fine copper precipitates (ε-phase) [20]. The small particles of this phase (<300Å) contain up to 96 wt% Cu [19]. Thus, the addition of more copper (≥2%) can also introduce precipitation hardening, and this is done in other types of stainless steel (ex.: 17-4PH martensitic steel). This strengthening mechanism is particularly useful for cast components that cannot be thermo-mechanically treated to achieve improved mechanical resistance. However, the effects of Cu addition on the localized corrosion performance of aged alloys in chloride media have yet to be sufficiently clarified, and

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there is some controversy in the literature regarding the effect of stainless steel composition and the experimental conditions (such as pH, temperature, and chloride concentration) used [21,22].

Therefore, this study investigated the effect of Cu addition on the corrosion resistance behavior and aging characteristics of duplex stainless steel as Cu content is added from 0 to 2.5% in highly concentrated sulfuric acid and chloride media.

2. Experimental Methods

2.1 Experimental alloys

The stainless steels evaluated in this study were prepared from commercially pure grade Fe, Cr, Ni, Mo, W, Cu, Fe-Si, Fe-Mn, and Fe-Cr-N. After being melted in a low-mid frequency vacuum induction furnace, only solid sections of the cast ingots were taken to prepare the specimens. The manufactured ingot was hot rolled to produce a 4 mm plate. The hot rolled specimens were annealed at 1,075 ºC for 10 min and then water quenched. A small section was cut after each procedure, and these sections were used for chemical analysis. Table 1 presents the chemical compositions of the experimental alloys. In addition, aging heat treatment was performed at 850 ºC for 30 min.

2.2 Microstructure analysis

Microstructure analysis was performed through optical microscopy and XRD analysis. Specimens for optical microscopic analysis were prepared by cutting them into pieces with the size of 1.5 × 1.5 cm. They were fixed in epoxy resin and polished using a SiC paper up to #2000. Then, diamond paste (1 μm) was used to give the specimen a mirror surface. After electrolytic etching (2V, 10 sec.) with 50 wt% KOH solution for microscopic observation, the microstructure was observed with an optical microscope (ZEISS AXIOTECH 100HD, Germany). The specimens for X-ray diffraction analysis were polished using SiC paper up to #600. 2θ was diffracted from 40º to 100º at a rate of 4º/min. In the case of annealing heat-treated specimens using XRD (RIGAKU's D/MAX 2000, Japan). To aging the heat-treated specimens, 2θ was diffracted from 40º to 55º at a rate of 1º/min.

2.3 Hardness measurement

The specimens were cut to pieces of size 1.5 × 1.5 cm, the surface of all specimens were ground with #120 grit SiC paper, and they were then measured in terms of hardness. The hardness meters used were the Rockwell hardness tester (JP/ATK-F1000, Japan) and C-scale.

2.4 Corrosion properties evaluation

2.4.1 Anodic polarization test

Specimens were cut into pieces of size 1.5 × 1.5 cm. Covered copper wire was connected to one of the specimen's faces using spot welding, then set using an epoxy resin. The surfaces of the specimens were polished using SiC paper up to #600. After the specimens were rinse, their surfaces were covered with epoxy resin with only 1 cm^2 of surface area being exposed to test solution. Specimens prepared in this way were kept in the desiccator until the test was initiated. The solutions were deaerated through purging with pre-purified nitrogen gas for 30 min at a rate of 200 mL/min prior to immersion of the specimen. The Potentiostat (Gamry Interface 1000, USA) was used in this experiment, where in the high-density carbon rod was applied as a counter electrode and the saturated calomel electrode was used as a reference electrode. The test solution was deaerated with (0.5N HCl + 1N NaCl) mixed solution and 6N H_2SO_4 solution. The scanning rate of potential was 1 mV/sec.

Table 1. Chemical composition of duplex stainless steels with different Cu contents (wt%)

Alloys	Cr	Mo	W	Si	Ni	Mn	C	Cu	N	P	S	Fe	α%	PRE_{30}
D2700	27.13	2.4	0.3	0.7	7.4	0.55	0.03	0.0	0.34	0.008	0.005	Bal.	38.4	45.8
D2708	27.10	2.4	0.3	0.8	7.1	0.62	0.02	0.8	0.37	0.008	0.005	Bal.	36.9	46.6
D2716	27.03	2.3	0.3	0.8	6.8	0.63	0.02	1.6	0.36	0.008	0.006	Bal.	38.1	45.9
D2724	26.94	2.4	0.2	0.8	6.6	0.64	0.02	2.4	0.39	0.008	0.006	Bal.	33.7	46.9

+ PRE_{30} = %Cr + 3.3(%Mo + 0.5%W) + 30%N

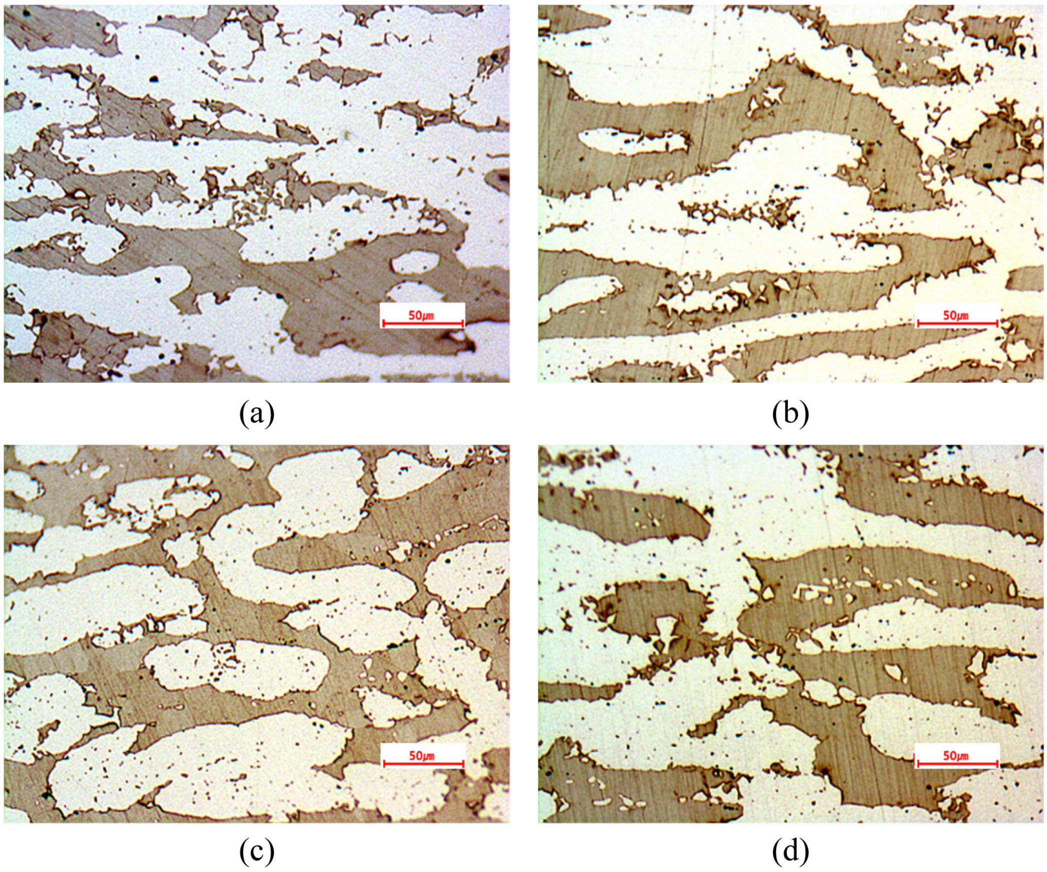


Fig. 1. Effect of annealing treatment (1075 ºC, 10 minutes) on microstructure of duplex stainless steels; (a) Cu 0%, (b) Cu 0.8%, (c) Cu 1.6%, (d) Cu 2.4%

3. Results and Discussion

3.1 Effect of Cu on the microstructure and corrosion properties of annealed duplex stainless steels

Fig. 1 shows the microstructure of solution-annealed alloy specimens at 1075 ºC for 10 min. The solution-annealed alloy specimens had a γ phase and an α phase. The γ phase can be seen as an isolated phase on the background of the α phase, which appears to be relatively white.

Fig. 2 shows the change in hardness according to the addition of Cu of duplex stainless steel. As the Cu content increases, the hardness also increases slightly. However, since copper has not a solid solution strengthening effect [22], it needs the further investigation even though the hardness was a value less than 27 HRC.

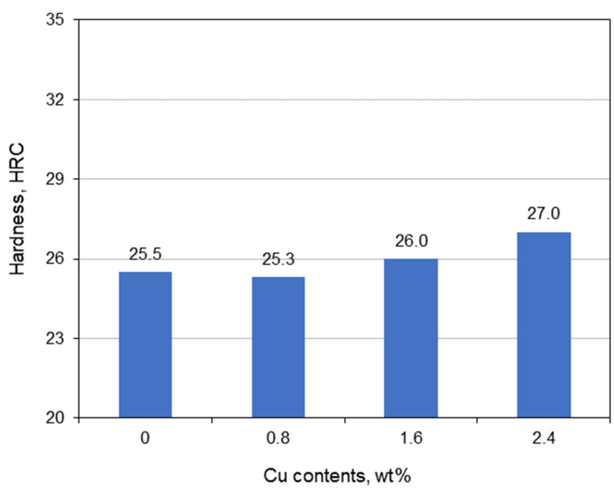


Fig. 2. Effect of Cu addition on hardness of annealed duplex stainless steels

Fig. 3 show the result of measuring the ferrite content. As the Cu content increased, it was found that the ferrite content decreased. It is determined that the alloying element Cu is an austenite stabilizing element [7], and the austenite region increases as the Cu content increases by stabilizing the austenite phase, whereas the ferrite region decreases.

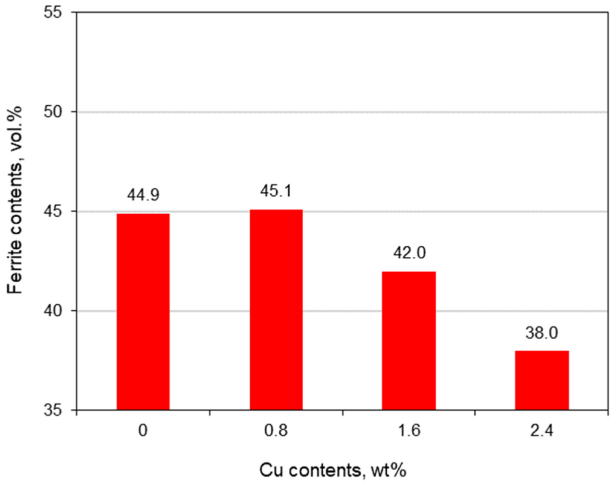


Fig. 3. Effect of Cu contents on ferrite volume percent in annealed duplex stainless steels

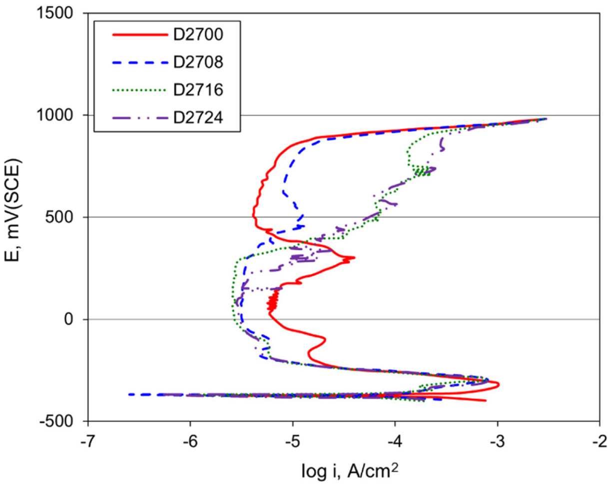


Fig. 4. Effect of Cu contents on the anodic polarization behavior of annealed duplex stainless steels in deaerated 0.5N HCl + 1.0N NaCl at 50 °C

To evaluate the corrosion resistance of the annealed duplex stainless steels, an anode polarization test was performed in chloride and sulfuric acid solutions. First, looking at the anodic polarization test in chloride, which are shown in Fig. 4, as the Cu content increased, the corrosion resistance increased in the low potential over the primary passive potential, while the corrosion resistance decreased in the high potential. Fig. 5 shows the passive current density at the low potential and at the high potential which have been obtained from Fig. 4. At the low passivation potential in the Fig. 5a, as the Cu contents increase, the passive current density

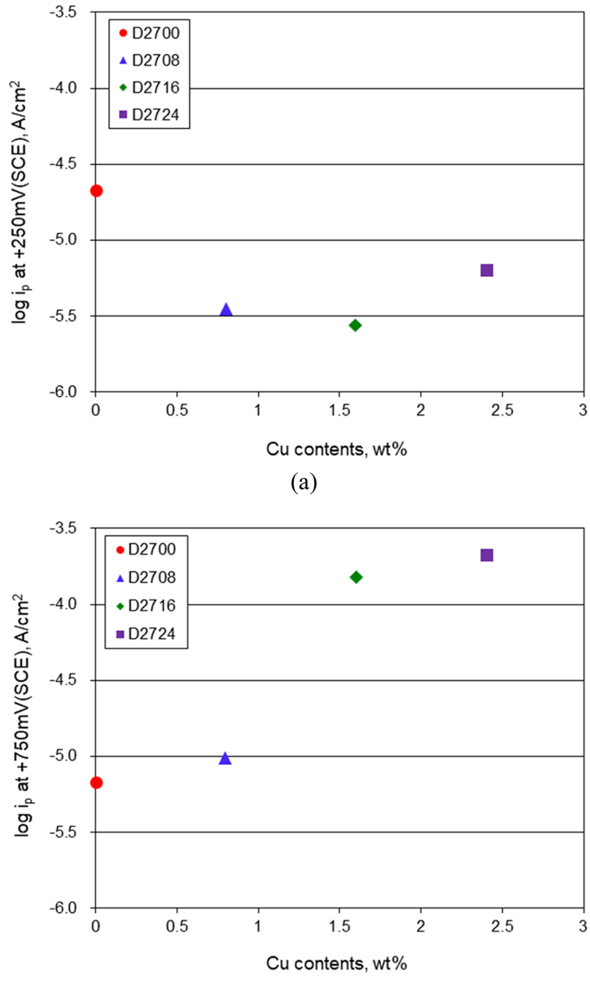


Fig. 5. Effect of Cu contents on corrosion indices of annealed duplex stainless steels in deaerated 50 °C, 0.5N HCl + 1.0N NaCl; (a) Passive current density at +250 mV(SCE), (b) Passive current density at +750 mV(SCE)

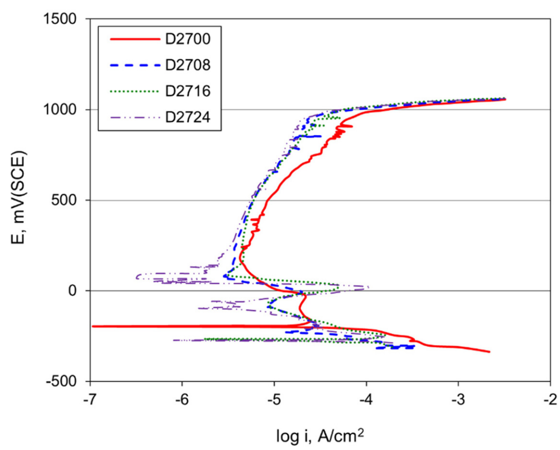


Fig. 6. Effect of Cu contents on anodic polarization behavior of annealed duplex stainless steels in deaerated 6N H_2SO_4 at 70 °C

decrease. However, at the high passivation potential in the Fig. 5b, as the Cu contents increases, the passive current density increases as well.

Fig. 6 shows the results of the anodic polarization test in sulfuric acid. As the Cu content increases, the anodic polarization behavior increases regardless of the passivation potential. Fig. 7 shows the passive current density at the low potential and at the high potential

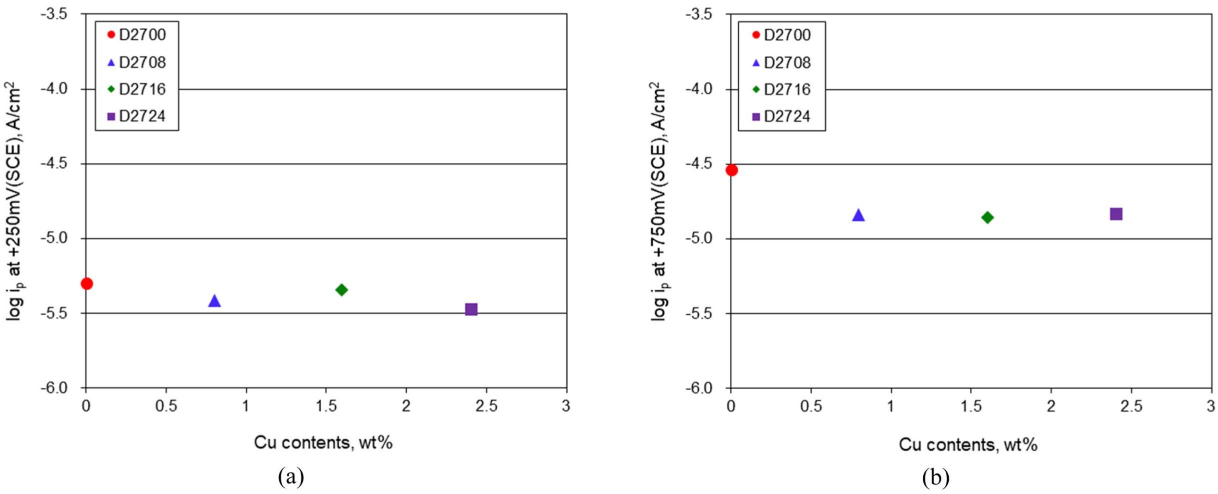


Fig. 7. Effect of Cu contents on corrosion indices of annealed duplex stainless steels in deaerated 70 °C, 6N H_2SO_4; (a) Passive current density at +250mV(SCE), (b) Passive current density at +750mV(SCE)

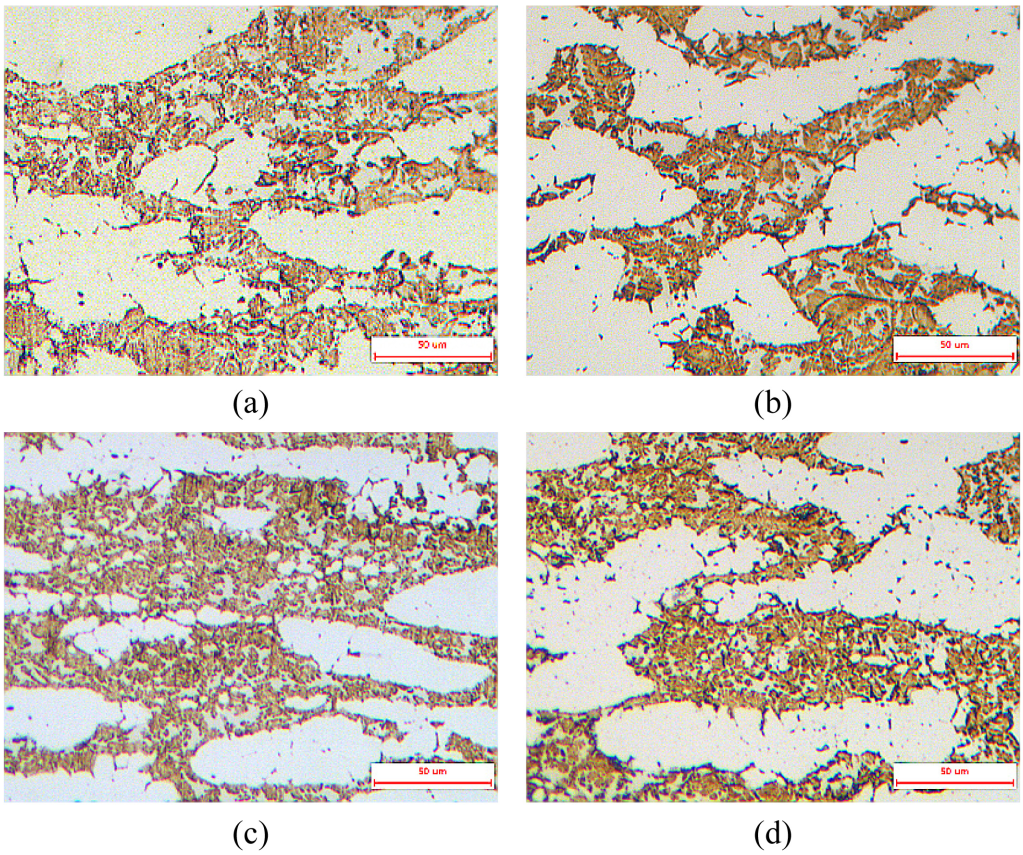


Fig. 8. Effect of aging treatment (850 °C-30min.) on microstructure of duplex stainless steels; (a) Cu 0%, (b) Cu 0.8%, (c) Cu 1.6%, (d) Cu 2.4%

obtained from Fig. 6. At the low passivation potential in the Fig. 7a, as the Cu content increases, the passive current density decreases slightly. Moreover, at the high passivation potential in the Fig. 7b, as the Cu contents increases, the passive current density decreases [6-10].

In summary, the Cu addition of annealed duplex stainless steel strengthened and reduced the ferrite contents of the alloys while it increased the polarization behavior in chloride or sulfuric solutions, except for in the case of high potential in chloride solution.

3.2 Effect of Cu addition on properties of aged duplex stainless steels

Fig. 8 shows the microstructure of the alloy specimens aged at 850 °C for 30 min. It can be seen in the Fig. that the decomposition of ferrite bands and secondary phases were precipitated in all alloys regardless of the Cu content.

Fig. 9 shows the hardness of duplex stainless steel that has been subjected to aging heat treatment and which shows a similar hardness regardless of the Cu content.

Fig. 10 shows the X-ray diffraction peak of aged duplex stainless steel. In addition to ferrite and austenite, secondary precipitation phases such as sigma and chi can be seen to exist in all alloys. The amount of secondary precipitated phases is visualized in Fig. 11 by obtaining the half-width of the XRD peak. Regardless of the Cu content, the generated sigma phase is about 2 times more than the chi phase, and the precipitation

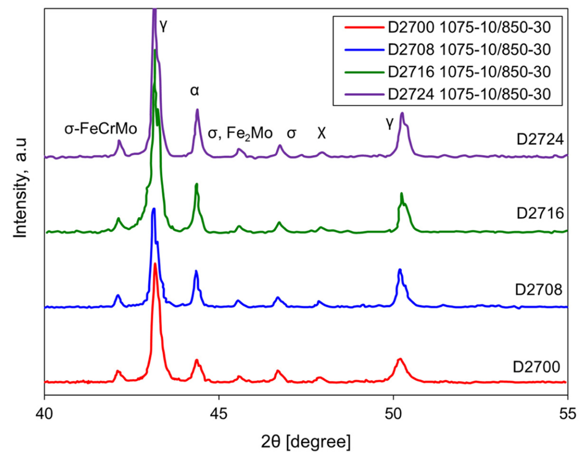


Fig. 10. Effect of Cu contents on XRD peaks of aged duplex stainless steels

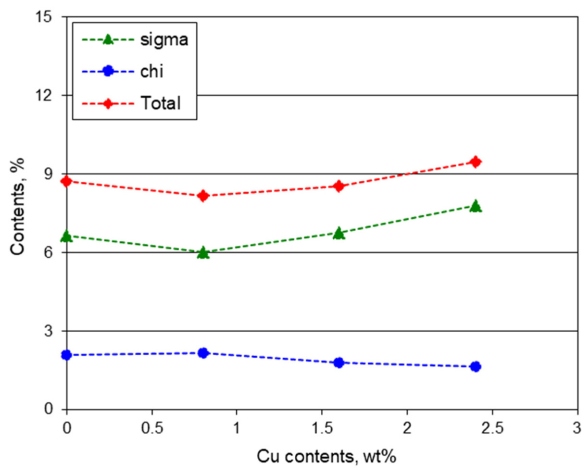


Fig. 11. Effect of Cu concentration on formation of sigma and chi phases in aged duplex stainless steels

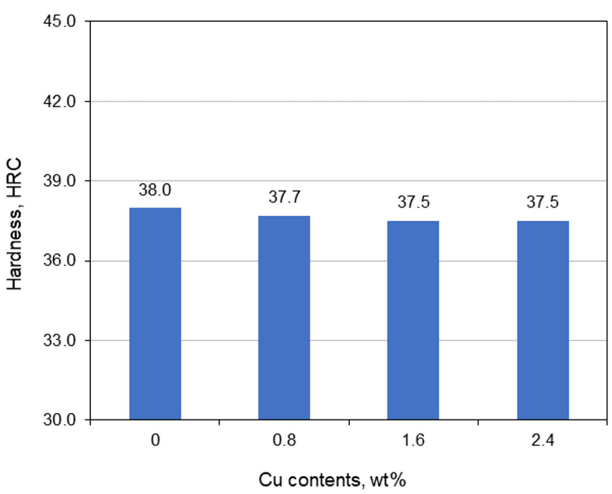


Fig. 9. Effect of Cu addition on hardness of aged duplex stainless steels

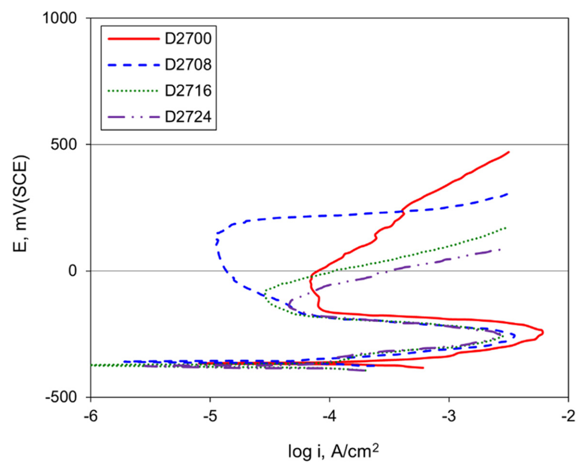
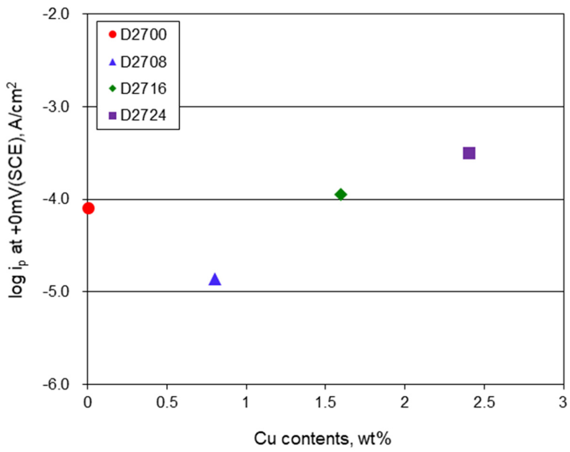
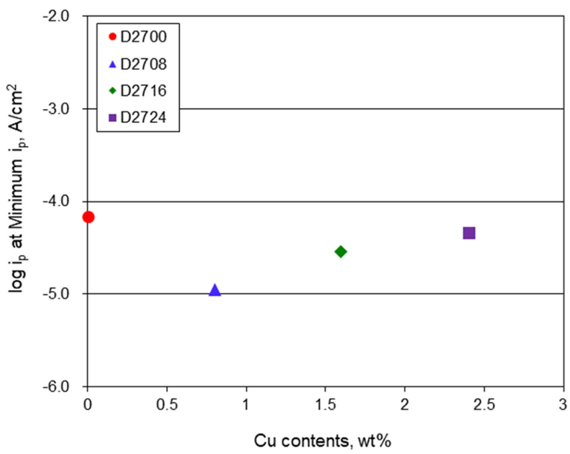


Fig. 12. Effect of Cu contents on anodic polarization behavior of aged duplex stainless steels in deaerated 50 °C, 0.5N HCl + 1.0N NaCl



(a)



(b)

Fig. 13. Effect of Cu contents on passive current density of aged duplex stainless steels in deaerated 50 °C, 0.5N HCl + 1.0N NaCl; (a) Passive current density at +0 mV(SCE), (b) Minimum Passive current density

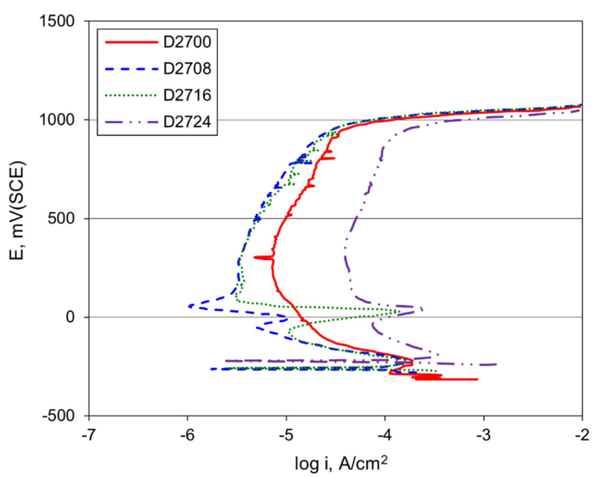
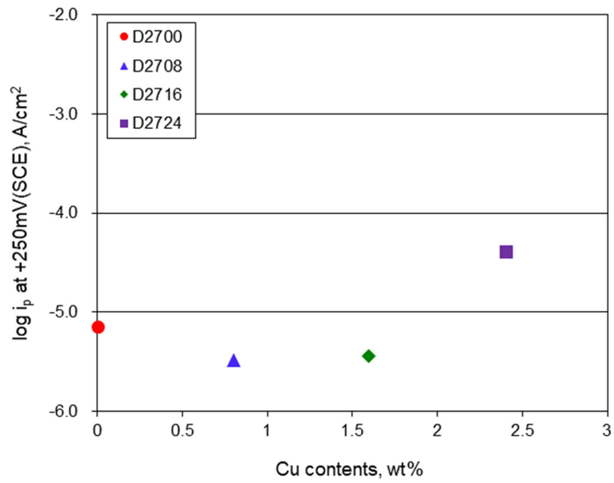
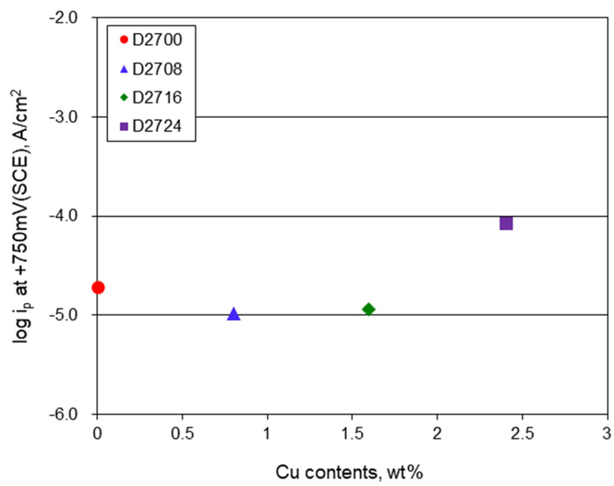


Fig. 14. Effect of Cu contents on anodic polarization behavior of aged duplex stainless steels in deaerated 6N H_2SO_4 at 70 °C



(a)



(b)

Fig. 15. Effect of Cu contents on passive current density of aged duplex stainless steels in deaerated 70 °C, 6N H_2SO_4; (a) Passive current density at +250 mV(SCE) potential, (b) Passive current density at +750 mV(SCE) potential

amount of the sigma phase reduced up to 0.8 wt% of the Cu content, and it then increased at 0.8 wt% Cu or more. The precipitation amount of kai phase was constant up to 0.8 wt% of the Cu content, and it then reduced at 0.8 wt% Cu or more. In summary, the formation of the harmful phases like sigma and kai by aging treatment reduced up to 0.8 wt% of the Cu content, then slightly increased at 0.8 wt% Cu or more.

To evaluate the corrosion resistance of aged duplex stainless steels, anodic polarization tests were performed in chloride and sulfuric acid solutions. First, the results of the anodic polarization test for chloride are shown in Fig. 12, where it can be seen that chloride has very low corrosion resistance compared to the annealed. Fig. 13 shows the passive current density at the low and high potentials. The passive current density at the low potential as shown in Fig. 13a reduced up to 0.8 wt% of the Cu content, and it then increased at 0.8 wt% Cu or more. As shown in Fig. 13b, the passive current density at the high potential reduced up to 0.8 wt% of the Cu content, and it then increased at 0.8 wt% Cu or more.

On the other hand, Fig. 14 shows the anodic polarization test results in sulfuric acid solution, which shows superior corrosion resistance compared to chloride. A stable and distinct passivation region is well observed in all alloys, but as can be seen in Fig. 15, when the Cu content exceeds 1.6 wt%, the passive current density regardless of the potential is reduced and the passive current density is increased at 1.6 wt% or more.

In summary, the Cu addition of aged duplex stainless steel reduced the formation of the harmful phases like sigma and kai and increased the polarization behavior in chloride or sulfuric solutions up to 0.8 wt% of the Cu content and it then slightly decreased at 0.8 wt% Cu or more.

4. Conclusions

The present study evaluated the effect of Cu addition on the microstructure, hardness, and corrosion behavior of duplex stainless steel in an acidic chloride and high-concentration sulfuric acid. The following conclusions were obtained.

(1) The Cu addition of annealed duplex stainless steel strengthened the alloy and reduced the ferrite contents of the alloy and increased the polarization behavior in chloride or sulfuric solutions, except for in the case of high potential in acidic chloride solution.

(2) The Cu addition of aged duplex stainless steel reduced the formation of the harmful phases like sigma and kai and increased the polarization behavior in acidic chloride or sulfuric solutions up to 0.8 wt% of the Cu content, and it then slightly decreased at 0.8 wt% Cu or more.

(3) The 0.8 wt% Cu addition to Fe-27Cr-7Ni-2.4Mo-0.3W-0.37N type duplex stainless steel was the optimum composition for the corrosion resistance of annealed or aged conditions.

Acknowledgments

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