Effects of Cu Addition on the Microstructure and Localized Corrosion Resistance of Hyper Duplex Stainless Steels Aged at 748 K

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The effects of Cu addition on the microstructure and localized corrosion of hyper duplex stainless steels aged at 748 K were investigated using TEM analysis and electrochemical test. The addition of Cu to the base alloy facilitated the precipitation of a Cr-enriched \( \alpha' \)-phase due to an increase in the Cr activity, thereby reducing the localized corrosion resistance. The localized corrosion was initiated at the Cr-depleted regions around the Cr-enriched \( \alpha' \)-phase.

(Received January 14, 2015; Accepted February 17, 2015; Published April 25, 2015)

Keywords: copper, stainless steel, scanning electron microscope (SEM), transmission electron microscope (TEM), localized corrosion

1. Introduction

Duplex stainless steel (DSS) has been used in various industrial applications for power plants, oil industries desalination facilities and chemical plants due to the excellent combination of high corrosion resistance and mechanical properties. It is well known that DSS has a dual microstructure, in which both ferrite (\( \alpha \)) and austenite (\( \gamma \)) phases are present in approximately equal volume fractions. DSS is relatively more economical than austenite stainless steel (ASS) due to the addition of low amounts of Ni.1,2,3

It is well recognized that super duplex stainless steels (SDSSs) such as UNS S32750 and UNS S32760 are defined with a pitting corrosion resistance equivalent number (PREN = Cr + 3.3 (Mo + 0.5 W) + 16 N \(^{4,5}\)) of 40–45. However, in a heat exchanger application, the pitting corrosion resistance of SDSSs with a PREN value above 40 is insufficient for higher temperature service, a long service life, or where materials with even higher corrosion resistance are needed.6,7 Hence, hyper duplex stainless steels (HDSSs) with a PREN value above 45 have been developed to provide high pitting corrosion resistance combined with excellent mechanical properties.8

It is well known that at 748 K, embrittlement occurs in most of the ferritic stainless steels (FSSs) or DSSs aged in a temperature range from 573 to 823 K.9 This embrittlement is caused by the formation of an \( \alpha' \)-phase within the \( \alpha \)-phase by nucleation and growth or by spinodal decomposition. The \( \alpha' \)-phase is rich in Cr and its structure is body centered cubic (bcc). The presence of an \( \alpha' \)-phase causes DSSs to be embrittled by decreasing the mobility of dislocations and the formation of microvoids near the dislocations in the \( \alpha \)-phase. Also, an \( \alpha' \)-phase decreases the pitting corrosion resistance of DSSs by the formation of a Cr-depleted zone around the \( \alpha' \)-phase.9,10 HDSS contains a significant amount of Cr, which improves corrosion resistance, and the presence of this element facilitates precipitation of a Cr-enriched \( \alpha' \)-phase. With the increased use of Cr as an alloying element in HDSS, the precipitation of a Cr-enriched \( \alpha' \)-phase has become more important.

In previous studies, the effects of alloying on the precipitation of the \( \alpha' \)-phase in DSSs were investigated. Trindade and Vilar11 reported that \( \alpha \)-phase decomposition was more pronounced after aging at 748 K with the addition of 2–4 mass% Ni to Fe-25 Cr and Fe-45 Cr alloys. Their results showed that the addition of Ni to the binary Fe-Cr alloy enhanced the kinetics of decomposition. Solomon and Levinson12 studied a series of duplex and single phase ferritic alloys to investigate the effects of Ni, Cu, Si, Mn and Mo on phase separation via Mössbauer spectroscopy and transmission electron microscopy. They found that the addition of both Ni and Cu promotes phase separation, but no effects of Mn, Si, or Mo on the phase separation kinetics could be found. Park and Kwon13 showed that replacing Mo with W in SDSS retarded the nucleation and growth rate of the Cr-enriched \( \alpha' \)-phase due to the slower diffusion rate of W as compared with that of Mo in the \( \alpha \)-phase, which resulted in increased pitting corrosion resistance in SDSS.

However, the effects of Cu addition on the precipitation of the \( \alpha' \)-phase and the associated localized corrosion resistance of HDSSs have not been clearly verified.

In this work, the effects of the Cu addition on the microstructure and localized corrosion of HDSSs aged at 748 K were investigated using a double-loop electrochemical potentiokinetic reactivation (DL-EPR) test, a scanning electron microscope-energy dispersive spectroscopy (SEM-EDS), a transmission electron microscopy (TEM) and a Thermo-Calc software.

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2. Experimental Procedures

2.1 Material and heat treatment

The experimental alloys with PREN 45 were prepared by melting commercial purity Fe, Cr, Mo, W, Ni, Cu, Fe-Cr-N, Si and Mn in a high frequency induction furnace. The 6 mm thick plate metal was solid solution heat treated for 30 minute at 1403 K followed by furnace cooling to 1373 K. Then, the alloy was solid solution heat treated for 15 min at 1373 K followed by water cooling. Table 1 shows the chemical compositions of the experimental alloys. To study the effects of the aging treatment, the alloys were aged for 10, 50 and 100 h at 748 K followed by water cooling.

2.2 Electrochemical test

The DL-EPR tests are carried out following the recommendations of Majidi and Streicher. The standard test solution (0.5 M H₂SO₄ + 0.01 M KSCN) was used for ASSs. On the other hand, a more aggressive solution (2 M H₂SO₄ + 0.01 M KSCN + 0.5 M NaCl) was used for the more corrosion resistant DSSs, 16)

However, in this work, in order to measure the degree of depletion of Cr around the α'- precipitation of the designed DSSs with aging at 748 K, a DL-EPR test was performed on the aged alloys in a deaerated 1.5 M H₂SO₄ solution (0.5 M H₂SO₄ + 0.002 M TA at 328 K instead of the above solution, using a saturated calomel electrode (SCE) using a specimen with an exposed area of 0.5 cm². The specimens were ground with 600-grit SiC abrasive paper. The degree of Cr-depletion in the alloys was evaluated by measuring the ratio of reactivation peak current (i_r) to activation peak current (i_a) when the potential was applied at a scan rate of 1 mV s⁻¹ from −500 to 200 mV_SCE, and then reversely to −500 mV_SCE.

2.3 Microstructural characterization

To examine the SEM images of the alloys, the alloys were ground to 2000 grit using SiC abrasive papers, polished with diamond paste. The sample was ultrasonic cleaned in acetone and distilled water to remove any impurities from the polished surface of the sample. An SEM was used to observe the sites of localized corrosion on the specimen after DL-EPR tests in a deaerated 1.5 M H₂SO₄ solution (0.5 M H₂SO₄ + 0.002 M TA at 1111). The DL-EPR tests in a deaerated 1.5 M H₂SO₄ solution (0.5 M H₂SO₄ + 0.002 M TA at 328 K instead of the above solution, using a saturated calomel electrode (SCE) using a specimen with an exposed area of 0.5 cm². The specimens were ground with 600-grit SiC abrasive paper. The degree of Cr-depletion in the alloys was evaluated by measuring the ratio of reactivation peak current (i_r) to activation peak current (i_a) when the potential was applied at a scan rate of 1 mV s⁻¹ from −500 to 200 mV_SCE, and then reversely to −500 mV_SCE.

2.4 Thermodynamic calculation

Thermodynamic calculations, using the Thermo-Calc software, were conducted in order to predict the effects of Cu on the activity of Cr, and calculation of the equilibrium state of system using the TCFE5-TCS steels/Fe-alloys database. The calculations were performed using the POLY and the POST modules in Thermo-Calc software. These modules are used in the calculation of complex heterogeneous equilibrium states and for plotting various kinds of phase diagrams and property diagrams.

3. Results and Discussion

3.1 Precipitation of the α'-phase at 748 K

TEM images from the alloys aged for 100 h at 748 K are shown in Figs. 1–3. Figures 1(a) and 2(a) show the α-phase and the α'/γ phase in the beam parallel to the (001) direction and to the (111) direction, respectively. In both cases, nanoscale α' were observed that seem to be associated with a spinodal decomposition of the α-phase to α- and α'-phases during the aging process. Diffraction pattern analysis revealed that the α'-phase has a body-centered cubic (bcc) structure. Close to the α/γ phase boundaries other precipitates, such as carbides and nitrides, were not observed (Figs. 1(b) and 2(b)). The experiments performed on the alloys aged at 748 K indicate that in these alloys phase separation of α into Fe-enriched α and Cr-enriched α' phases takes place via a nucleation and growth mechanism. TEM-EDS analyses (Fig. 3) have been conducted in different regions. Precipitates are richer in Cr than the ferrite region without precipitates, as can be seen from a comparison.
between the concentration of the ferrite region without precipitates and that of the precipitates. Obviously, the depletion of Cr is more pronounced near the precipitates in the ferrite regions.

A Vickers hardness test of the alloys was performed on the α- and γ-phases in order to elucidate the effects of Cu addition and increasing of the aging time at 748 K on the hardness associated with the precipitation of the α'-phase (Fig. 4). With the addition of Cu to the alloy and increasing of the aging time, the Vickers hardness of the α-phase increased, thereby increasing the hardenability of the sample. However, there was no change in the hardness of the γ-phase, irrespective of the addition of Cu to the alloy.

In previous studies, the Vickers hardness test showed that the hardening might be due to the precipitation of the α'-phase. An increase in the micro-hardness of the α-phase is known to be associated with the local Cr-enrichment caused by the spinodal decomposition or the α'-phase precipitation in the γ-phase.

In summary, the addition of Cu to the BASE alloy facilitates α-phase hardening due to the accelerated precipitation of the α'-phase.

3.2 The DL-EPR behavior

It is well known that the DL-EPR test is used to estimate the degree of sensitization of stainless steels. It selectively focuses on the matrix around fine precipitates formed during aging, rather than the precipitates themselves. Shultze et al. proposed that a DL-EPR test carried out in 0.5 M H$_2$SO$_4$ + 0.001 M TA, to measure the degree of depletion of Cr around the α'-phase formed in experimental DSSs aged at 748 K. However, in this work, the test was performed in a modified solution of 1.5 M H$_2$SO$_4$ + 0.002 M TA at 328 K.

As shown in Fig. 5, it should be noted that while the anodic and cathodic curves intersect at a single corrosion potential during forward scanning, during backward scanning, the cathodic curve crosses the anodic curve at three different corrosion potentials, first one in the passive state, the second one in transition, and the third one in the active state. As a result, four regions (a), (b), (c), and (d) are formed...
in the reactivation stage where a and c are affected by absolute anodic current, while b and d are affected by absolute cathodic current (Fig. 5(a)). Therefore, to calculate the degree of sensitization, the summation of anodic current in the regions a and c was considered. The results of the DL-EPR tests can be divided into four sensitivity groups corresponding to following sequence proposed by Cihal. If the $i_r/i_a$ ratio falls within the ranges $0 \sim 2\%$, $2 \sim 8\%$, $8 \sim 30\%$, $>30\%$, then the samples are classified as no sensitization (method sensitivity threshold is 2\%), trace sensitization, weak-to-medium sensitization, and severe sensitization, respectively.

In Fig. 6, while the BASE and CU15 alloys are classified as no sensitization in the solid solution heat treatment, both alloys aged at 748 K for 10 h are classified as weak (10.6\%) and medium sensitization (19.3\%), respectively. In the case of alloy aging at 748 K for 100 h, the CU15 alloy is classified as severely sensitization (37.25\%), but the BASE alloy is classified as medium sensitization (25\%). The degree of Cr-depletion with aging for the alloys is represented by the ratio of the $i_r/i_a$ ratio. This ratio is much higher for the CU15 alloy than for the BASE alloy when they are equivalently aged, which demonstrates that the degree of Cr-depletion is greater in the CU15 alloy than in the BASE alloy due to the facilitation of $\alpha'$-phase precipitation.

In summary, with the addition of Cu to the alloy and increasing of the aging time at 748 K, $i_r/i_a$ ratio increased due to an increase of the Cr-depleted areas around the Cr-enriched $\alpha'$-phase, thereby decreasing the resistance to pitting corrosion.

3.3 The effect of Cu addition on the precipitation of the $\alpha'$-phase at 748 K

It is well known that a spinodal decomposition process in the $\alpha$-phase forms the $\alpha'$-phase during aging. In the Fe-Cr system, the $\alpha$-phase may decompose into an Fe-enriched $\alpha$-phase and a Cr-enriched $\alpha'$-phase by a miscibility gap. The $\alpha'$-phases contained much higher amounts of Cr as compared to the matrix of the cast DSSs as determined by applying TEM-EDS on extraction replicas. There are reports that a Cr-enriched phase, which has a bcc lattice, allows its identification as an $\alpha'$-phase, and that a Cr-enriched $\alpha'$-phase
The effect of Cu addition on the activity of Cr can be calculated as a function of Cu content as shown in Fig. 8. Cr activity increases with an addition of Cu content. In the experimental alloys, since Cr is a main element of the Cr-enriched $\alpha'$-phases, the addition of Cu to the alloy increases the precipitation rate of the $\alpha'$-phases due to increasing of Cr activity.

Acknowledgements

This work has been supported by Ministry of Knowledge Economy of the Republic of Korea and by the Global Research Laboratory Program of Korea Ministry of Education, Science and Technology.

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