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# Corrosion Science

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## ABSTRACT

To elucidate the effects of Cu on the precipitation of intermetallic compounds and the intergranular corrosion of the hyper duplex stainless steels, a double loop potentiokinetic reactivation test, a scanning electron microscope analysis and thermodynamic calculation were conducted. The addition of Cu to the base alloy reduces the total amount of intermetallic compounds. Particularly, Cu addition to the base alloy results in pronouncedly suppressing the amount of sigma phase whereas it slightly increases chi phases. The Cu added alloy reduces the degree of sensitization due to the delayed precipitation of intermetallic compounds, compared with that of the base alloy.

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### 1. Introduction

Duplex stainless steel (DSS) is the stainless steel that has microstructure where both ferrite ( $\alpha$ ) and austenite ( $\gamma$ ) phases are present in approximately equal volume fraction. In general, it is well known that standard stainless steel such as UNS S32205 is defined as DSS with a pitting resistance equivalent number (PREN = Cr + 3.3 (Mo + 0.5 W) + 16 N [\[1,2\]\)](#page--1-0) of 35 and super duplex stainless steels (SDSSs) such as UNS S32750, UNS S32760 and UNS S32550 are defined as DSSs with PREN of 40–45. SDSSs have been increasingly used for various applications such as power plants, desalination facilities and chemical plants due to high resistance to pitting and crevice corrosion, excellent mechanical properties and a relatively low cost, compared with other higher performance materials such as super austenite stainless steel (SASS) [\[3–5\].](#page--1-0)

However, in heat exchanger application, corrosion resistance of SDSS is insufficient for higher temperature service or for a long service life, and where materials, with even higher corrosion resistance, are needed. Hyper duplex stainless steel (HDSS) such as UNS S32707 is defined as a highly alloyed duplex stainless steel with a PREN in excess of 45 [\[1\].](#page--1-0) HDSSs were developed to meet industry demands for higher operating temperatures and longer run times and replace the costly SASS that has high levels of Ni and Mo contents [\[6,7\].](#page--1-0) The existing researches were progressed for DSS and SDSS [\[8–12\]](#page--1-0). However, few studies have been focused

on HDSS, having higher Cr, Mo and W than DSS and SDSS, to substitute the 6% Mo austenite stainless steels (ASSs) in more severe environment.

The intermetallic phases such as sigma ( $\sigma$ ) phase and chi ( $\chi$ ) phase are the intermetallic phases that forms at high temperature 600–950 °C [\[13,14\]](#page--1-0). These intermetallic phases lower the fracture toughness and the corrosion resistance significantly [\[15–17\].](#page--1-0) To avoid this embrittlement and corrosion, DSSs are subjected to solution heat treatment followed by water quenching in the final stage of production or fabrication. The PREN 40 grade SDSS (e.g. UNS S32750) contains larger amounts of Cr and Mo than the PREN 35 grade DSS (e.g. UNS S32205), and as a result, has a tendency to precipitate the intermetallic phases.

According to time–temperature-transformation (TTT) curve [\[18,19\]](#page--1-0), the PREN 40 grade SDSS precipitates 1%  $\sigma$  phase after aging for 100 s at 850  $\degree$ C whereas the PREN 35 grade DSS precipitates 1%  $\sigma$  phase after aging for 2000 s at 850 °C. That is, the precipitation rate of the  $\sigma$  phase in the PREN 40 grade is much faster than that in the PREN 35 grade. If the furnace to quench time and quench rate is not sufficient, these brittle  $\sigma$  phases in the center of large sections of the PREN 40 grade SDSS can be easily precipitated. In reality, these brittle  $\sigma$  phases in the PREN 40 grade SDSS with heavier section have been observed to be forming during the cooling process after the continuous casting, during the slow cooling process of hot rolling, in the center of a casting, and in the heat affected zone after welding.

The effect of addition of various elements on the precipitation of secondary phases has been investigated. Park et al. [\[20\]](#page--1-0) assumed that the addition of rare earth metals suppress the precipitation



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## Table 1

Chemical composition of the experimental alloys (wt.%).



 $*$ PREN = Cr + 3.3 (Mo + 0.5 W) + 16 N.



Fig. 1. Optical micrograph of the experimental alloys after solution heat-treated at 1090 °C for 30 min: (a) the alloy-WBASE and (b) the alloy-WCU.



Fig. 2. BSE images of the experimental alloys at 850 °C for 10 and 30 min: (a) the alloy-WBASE and (b) the alloy-WCU.

of the  $\sigma$  and  $\chi$  phases in SDSS, because the REM (rare earth metals) atoms occupy the vacancies, effectively limiting the diffusion of Cr, Mo and W and REM oxides/oxy-sulfides which acts as the obstacles seemed to enhance the retardation effect. Huang et al. [\[21\]](#page--1-0) showed that the higher the N content, the lower  $\sigma$  phase content in DSSs. However, Si addition retards  $\delta$  phase decomposition into the  $\gamma$ phase when SUS 309L stainless steels are solution treated at 1050 °C and also enhances the  $\delta$ -ferrite decomposition rate and accelerates  $\sigma$  phase precipitation [\[22\]](#page--1-0).

Ogawa et al. [\[23\]](#page--1-0) showed that W in the HAZ of DSS is effective in delaying  $\sigma$  phase precipitation due to the enhancement the tendency to form the  $\chi$  phase with a higher nucleation efficiency and lower growth rate than the  $\sigma$  phase. Kim et al. [\[24\]](#page--1-0) showed that a partial substitution of W for Mo in DSS retarded the formation of  $\sigma$  phase in the alloys. Park et al. [\[25\]](#page--1-0) reported that a partial substitution of W for Mo in ferritic stainless steels (FSSs) not only increased resistance to pitting corrosion of the alloys by a synergic contribution of Mo and W but also reduced the amount of

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