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Influence of the addition of gadolinium on the microstructure and mechanical properties of duplex stainless steel

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ABSTRACT

The aim of this study is to investigate the effects of gadolinium addition on the microstructure and mechanical properties of duplex stainless steel (DSS) fabricated using a normal casting method. The oxygen content in the cast DSS alloy with gadolinium decreased because of the high reactivity of gadolinium with oxygen. The area fraction and size of non-intermetallic inclusions in the alloy decreased from $0.80 \pm 0.12\%$ to $0.58 \pm 0.04\%$ and from 6.9 ± 0.7 to 5.8 ± 0.4 μm upon gadolinium addition, respectively. Notably, the ultimate tensile strength and strain at break of the cast alloy significantly increased with the addition of gadolinium from 919 ± 25 to 969 ± 8 MPa and from $24.8 \pm 1.9\%$ to $28.4 \pm 1.1\%$, respectively. The hardness of the cast alloy with gadolinium increased from 23.6 ± 1.3 to 25.0 ± 1.2 HRC. A significant increase in the impact energy of the cast alloy was observed and the brittle-to-ductile transition temperature slightly decreased by approximately 10 °C with the addition of gadolinium.

1. Introduction

Duplex stainless steels (DSSs), which comprise ferrite (α) and austenite (γ), have been widely investigated because of their favorable mechanical properties and corrosion resistance [1–3]. DSS has higher strength and better stress corrosion and pitting and crevice corrosion resistance than pure austenitic grades [4,5]. With its combination of excellent corrosion resistance and tensile strength, DSS can be used in a variety of applications including oil, pulp and paper, petrochemical, and marine industries [1,6,7].

While chromium (Cr), molybdenum (Mn), and nickel (Ni), the main components of DSS, make DSS strong and corrosion-resistant, they also form detrimental tertiary phases such as sigma (σ) phases that only appear in ternary Fe–Cr–Mo systems and chi (χ) phases that are present in ternary Fe–Cr–Mo and quaternary Fe–Cr–Ni–Mo systems [8–11]. These intermetallic σ and χ phases have negative effects on the corrosion and mechanical properties of DSS because of embrittlement [12,13]. Previous studies by other groups reported that the precipitation of the σ phase occurs when steels are annealed below 1000 °C, and it can be removed using a solution treatment process that provides control of the ferrite and austenite proportions [14–19]. Moreover, non-metallic inclusions in steel are detrimental to the corrosion and mechanical properties [20–22]. In particular, owing to their brittle character, they cause crack formation and fatigue failure in steel during deformation processes such as forging and flattening [23]. For instance, nitrogen, which is used to strengthen DSS, reacts with other elements with high affinity to nitrogen and forms nitrides such as Cr_2N. Further, oxides that are detrimental to corrosion properties can form during the manufacturing process. Therefore, various attempts have been made to produce high-quality DSS by inhibiting the formation of intermetallic phases and non-metallic inclusions.

Recently, the addition of rare earth metals to stainless steel has shown to reduce the formation of intermetallic phases and non-metallic inclusions [24,25]. Some researchers have also demonstrated that the addition of rare earth metals to steel promotes solid solution hardening and suppresses the formation of precipitates, such as σ phases, by occupying voids and vacancies in the ferrite matrix and reducing the diffusion rates of the elements involved in precipitate formation [26–30]. In addition, the standard free energies of formation for rare earth oxide and sulfide formation are lower than those for other non-metallic inclusions, such as manganese sulfide (MnS) and chromium oxide (Cr_2O_3); therefore, the addition of rare earth metals can retard the deleterious actions of non-metallic inclusions [24]. The addition of cerium (Ce), a representative rare earth metal, to steels has shown to improve their mechanical and corrosion properties [24–26,31]. Kim et al. and Jeon et al. reported that pitting corrosion resistance was enhanced following the addition of Ce to DSS [25]. Liu et al. revealed that the sizes and morphologies of non-metallic

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inclusions and the mechanical properties of 2205 DSS were positively changed after adding Ce [23,32].

Gadolinium (Gd) is one of the more abundant rare earth metals and has special characteristics such as a high neutron cross-section [33]. It has been used in neutron therapy applications for targeting tumors, and recently, it has been introduced as a neutron absorber material for the shielding of nuclear fuels in nuclear reactors [34]. DSS, when successfully fabricated with Gd addition, may benefit from these characteristics through enhancement of its corrosion resistance and mechanical properties and be ideally suited for a variety of applications in the nuclear industry.

The present study thus focuses on investigating the influence of Gd on the microstructure and mechanical properties of DSS. DSS with a pitting resistance equivalent number (PREN = wt% Cr + 3.3 wt% Mo + 30 wt% N) of 50 was used [25] and 0.1 wt% of Gd was added to DSS and alloyed through casting, and the microstructure and inclusions in the alloy were investigated via field emission scanning electron microscopy (FE-SEM) and x-ray crystallography (XRD). The mechanical properties were examined using Charpy impact, hardness, and tensile strength tests.

2. Experimental procedure

2.1. Materials and production

Commercially available high-purity iron (Fe), chromium (Cr), nickel (Ni), manganese (Mn), silicon (Si), ferro-molybdenum (Fe-60 wt% Mo), and ferrochromium nitride (Fe-60 wt%Cr-10 wt%N) were used as the starting materials. The investigated alloys were fabricated using a high-frequency induction melting furnace (Inductotherm, USA). To prevent Gd oxidation, all of the metals except Gd were first melted at 1630 °C and then gadolinium particles (0.1 wt%, 1–2 mm, 99.99%, Treibacher industrie, Germany) were added to the melted alloy in the ladle at 1580 °C.

The cast alloys were cut into 230 mm × 30 mm × 30 mm blocks and solution treated at 1130 °C for 120 min followed by quenching in water to achieve an approximate 45:55 ratio of ferrite and austenite. Fig. 1 shows the temperature profile of the heat treatment used in our experiment. Table 1 shows the chemical compositions and PREN levels for the fabricated alloys with and without added Gd determined using inductively coupled plasma optical emission spectroscopy (ICP-OES, iCAP-6300, Thermo Scientific, Germany). The formation free energies of gadolinium compound were calculated with HSC thermodynamic software.

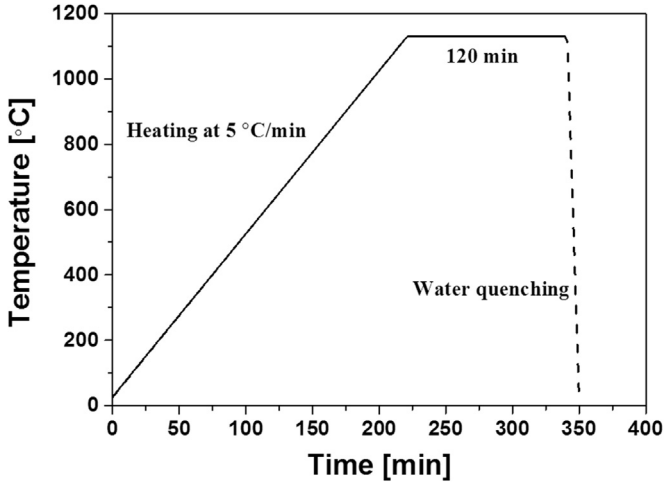

Fig. 1. Schematic diagram of the heat treatment used to solution treat the alloy to achieve an approximate 45:55 ratio of ferrite and austenite.

For simplicity, the alloy without Gd is referred to as Alloy I and the alloy with Gd as Alloy II.

2.2. Microstructure characterization

The annealed samples for microstructure observations were ground with 2000-grit SiC sand paper and polished using alumina suspension slurries. The analyses of the two DSS alloys with and without added Gd were accomplished using the back-scattered electron (BSE) mode of a Quanta 200 F FE-SEM (FEI Company, USA) before and after solution treatment. An energy dispersive spectroscope (EDS) attached to the FE-SEM was also utilized to analyze the chemical compositions of the samples. The phases of the alloys were characterized via x-ray diffraction (XRD, D8-discover, Bruker, Germany) analysis using monochromatic Cu Kα radiation. The specimens were scanned over a diffraction angle range from 10° to 110° at a scanning rate of 0.1°/min. The percentage of ferrite phase was determined using a feritscope (FMP-30, Fischer, Germany) with a 0.1% ferrite detection limit. On average, 30 fields per specimen were analyzed. The average sizes and areas of the inclusions in the alloys were evaluated using an inclusion analyzer (CTR 6000, Leica, Germany).

2.3. Mechanical properties

Tensile strength, Charpy impact, and hardness evaluations were performed to study the mechanical properties of the DSS alloys with and without added Gd. Cylindrical specimens were elongated at a constant cross-head speed of 2 mm/min according to the ASTM-A370 test method to determine their tensile properties (AG-X 300KN, Shimadzu, Japan). The Charpy impact test was performed according to the KS-0809 standard on V-notched specimens ($10 \times 10 \times 55$ mm^3) using a Charpy-type impact tester (SA-ID3, Satec, USA) in a temperature range from −100 to 100 °C. The fractured surfaces of the specimens after testing were examined via FE-SEM. The Vickers hardness test was conducted using a Rockwell hardness tester (Series 500, Wilson, USA). The applied load and holding time were 150 kgf and 3 s, respectively. On average, 20 fields per specimen were analyzed.

Each mechanical test was performed on more than five specimens of each alloy to obtain statistically significant results. All quantitative data are reported as mean ± standard deviation values. One-way ANOVA was used to compare the statistical analyses, and $p < 0.05$ was considered significant.

3. Results and discussion

3.1. Microstructure of alloys

The cast alloys were well fabricated without any noticeable cracks using an air casting method. The targeted PREN value was approximately 50 for all alloys. PREN equation used in this study is modified from the equation Lorenz and Medawar suggested for austenitic stainless steels and austenitic phase in duplex stainless steel [25,35]. The modification of the equation is from taking into account of the solubility of nitrogen in ferrite phase in DSS as well as the change in the partitioning coefficients of Cr and Mo [36,37].

The chemical compositions of the alloys were close to the targeted compositions. It should be noted that while 0.1 wt% Gd was added to Alloy II, the ICP analysis indicated the presence of just 0.015 wt% Gd, as shown in Table 1. The oxygen content of Alloy I was 0.0684 wt%, while that of Alloy II was 0.0574 wt%, which is 16% lower than that of Alloy I. The noticeably low Gd and oxygen contents in the cast alloy are likely because of Gd acting as a deoxidizing agent during air casting, which caused Gd-oxide slag