Aging Effect on Mechanical Behavior of Duplex Satinless Steel

Jungho Moon, Tae Kwon Ha

Abstract—Effect of alloying on the microstructure and mechanical properties of heat-resisting duplex stainless steel (DSS) for Mg production was investigated in this study. 25Cr-8Ni based DSS's were cast into rectangular ingots of which the dimension was 350×350×100 mm³. Nitrogen and Yttrium were added in the range within 0.3 in weight percent. Phase equilibrium was calculated using the FactSage®, thermodynamic software. Hot exposure, high temperature tensile and compression tests were conducted on the ingots at 1230°C, which is operation temperature employed for Mg production by Silico-thermic reduction. The steel with N and Y showed much higher strength than 310S alloy in both tensile and compression tests. By thermal exposition at 1230°C for 200 hrs, hardness of DSS containing N and Y was found to increase. Hot workability of the heat-resisting DSS was evaluated by employing hot rolling at 1230 °C. Hot shortness was observed in the ingot with N and found to disappear after addition of Y.

Keywords—Duplex Stainless Steel, alloying elements, eutectic carbides, microstructure, aging treatment.

I. INTRODUCTION

MAGNESIUM is usually produced by the Silico-thermic reduction known as Pidgeon process [1], in which magnesium ore (dolomite) is reduced in the reactor called retort. Since the reduction of dolomite is carried out at high temperature (1200~1250°C) and high vacuum (1~10 Pa), the materials used as retort are required heat resisting characteristics such as high resistance to oxidation and sulphidation attack, high strength and comprehensive mechanical properties, good stability of high temperature microstructure above 1200°C [2]. Good welding performance and handling characteristics are also needed. During magnesium smelting, common failure modes of the retort can be categorized into two cases: one is through cracking and deformation, depression, post-cracking deformation; the other is the oxidation of cracks. In this regard, duplex stainless steels of high Ni contents have been employed as retort materials in magnesium production.

Duplex stainless steels have a mixed structure of BCC ferrite and FCC austenite. The exact amount of each phase is a function of composition and heat treatment. Most alloys are designed to contain about equal amounts of each phase in the annealed condition. The principal alloying elements are chromium and nickel, but nitrogen, molybdenum, copper, silicon, and tungsten may be added to control structural balance and to impart certain corrosion-resistance characteristics. The specific advantages offered by duplex stainless steels over conventional 300-series stainless steels are strength (about twice that of austenitic stainless steels), chloride stress corrosion cracking (SCC) resistance, and pitting corrosion resistance [3]. These materials are used in the intermediate temperature range (about -60 to 300°C) where resistance to acids and aqueous chlorides is required. Duplex stainless steels have found widespread use in a range of industries, particularly the oil and gas, petrochemical, pulp and paper, and pollution control industries.

In the present study, it has been attempted to apply 25Cr-8Ni based duplex stainless steel, relatively lower level of Ni, containing N and Y to magnesium reduction, where both high strength and oxidation resistance at temperatures above 1200°C are required at the same time. Five ingots were cast in this study for this purpose. For comparison, ingot of 310S, typical heat resisting austenitic stainless steel, was also cast in this study. Microstructure observation and hardness tests after hot exposure at 1230°C for up to 200 hrs, high temperature tensile and compression tests were carried out. Hot workability was evaluated by employing hot rolling test at 1230°C. Thermodynamic calculation for phase equilibrium has also been carried out and the effect of nitrogen addition has been analyzed.

II. EXPERIMENTAL PROCEDURES

Duplex stainless steels with chemical compositions listed in Table I were cast by vacuum induction melting (VIM) into the ingots with dimensions of 350 mm × 350 mm × 100 mm. Ingot No. 5 is 310S stainless steel. The appearance of an ingot was illustrated in Fig. 1. The ingots were solution heat treated at 1200°C for 2 hrs followed by furnace cooling. Microstructure observation revealed primarily austenite, ferrite, and some carbides precipitated along grain or phase boundaries. To predict thermodynamically stable phases and their fractions, phase equilibrium was calculated with FactSage® and database of FSStel®.

After cutting the ingots longitudinally, microstructure of the duplex stainless steels was observed using optical microscopy and scanning electron microscopy. To investigate the stability of microstructure, aging treatment was conducted at 1230°C for 1 to 200 hrs, followed by microstructure observation and hardness tests. Etchant consisting of 3 parts Nitric acid, 2 parts Hydrochloric acid and 1 part distilled water was used. Hardness

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was measured by Rockwell B scale using 100 kgf load. Tensile and compression test specimens were also machined along longitudinal direction, of which the dimensions were 8 mm in diameter and 10 mm in gage length in both cases. Tensile and compression tests were carried out at 1230°C and at the strain rate of 5×10^{-4}/s using ThermacMastor®. Heating rate was 10°C/min and the specimens were rapidly cooled by blowing nitrogen gas after each test.

TABLE I
CHEMICAL COMPOSITIONS OF THE INGOTS PRODUCED IN THIS STUDY. (WT.%)

Ingot	Cr	Ni	Si	N	Y	Mn	C	Fe
1	25	8	1.5	-	-	1.0	0.4	Bal.
2	25	8	1.5	0.3	-	1.0	0.4	Bal.
3	25	8	1.5	-	0.3	1.0	0.4	Bal.
4	25	8	1.5	0.3	0.3	1.0	0.4	Bal.
5	25	20	1.5	-	-	1.0	0.1	Bal.

Hot workability of as-cast ingots was evaluated in this study by performing hot rolling at 1230°C. For each pass, thickness reduction of 10% was subjected and the surface was inspected to check cracking. Microstructure was also observed after hot rolling experiments.

III. RESULTS AND DISCUSSION

Fig. 2 is the results obtained from thermodynamic calculation using FactSage® and showing stable phases and their fractions. It is apparent that main constituent phases are FCC austenite and BCC ferrite and that the carbides can form even from the liquid phase. Interestingly, with addition of nitrogen, fraction of austenitic phase at high temperature obviously increases and Cr_2N is expected to precipitate simultaneously with carbides from above 1100°C. Equilibrium fraction of BCC ferrite is above 0.6 at room temperature and sigma phase is expectedly to form at 700°C and disappear below 530°C, which is very important phase determining mechanical property of duplex stainless steel during not only fabrication but also application [4].
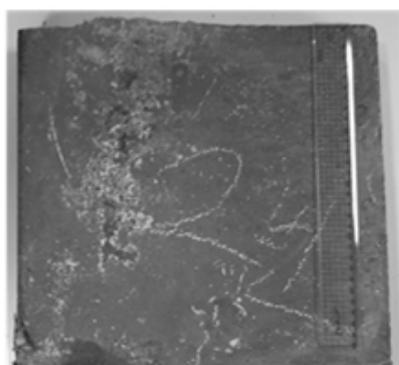
Fig. 1 Appearance of the ingot fabricated in this study

Nitrogen has a multiple effect on stainless steels by increasing pitting resistance, austenite content and strength [5]. This effect is enhanced in the presence of Mo and it has been suggested that Mo and N have a synergistic influence on pitting characteristics [6]. Nitrogen partitions preferentially to the austenite due to the increased solubility in the phase and also

concentrates at the metal-passive film interface [7]. During prolonged passivation of stainless steels in acid solutions, surface nitrogen enrichment has been witnessed, which explains how nitrogen can influence repassivation. Nitrogen has also been noted to increase the crevice corrosion resistance, which is due to nitrogen altering the crevice solution chemistry or by segregating to the surface, which is in keeping with the mechanism for enhanced pitting resistance [3].
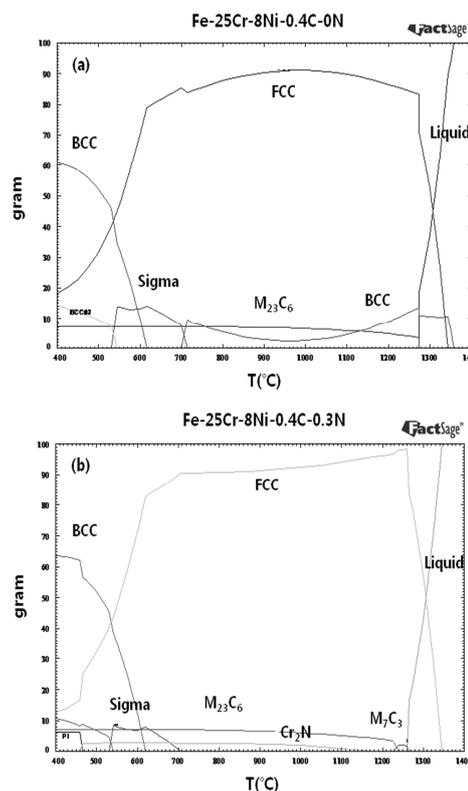
Fig. 2 Calculated phase equilibria showing stable phases and their fractions for (a) alloy No. 1 and (b) No.
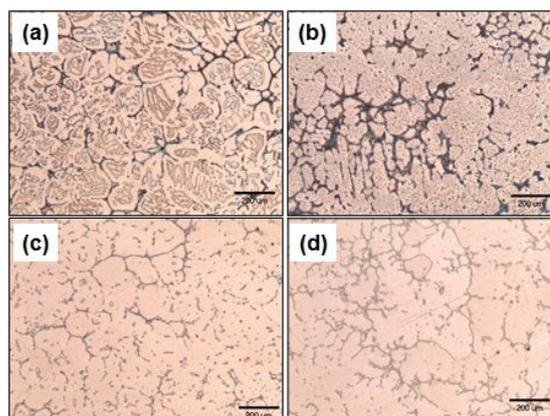
Fig. 3 Optical micrographs showing as-cast microstructures of the ingot (a) No.1, (b) No.2, (c) No. 3 and No. 4, fabricated in this study

Another important property of nitrogen is its ability to stabilize duplex alloys against the precipitation of intermetallic phase, such as sigma and chi, by reducing Cr-partitioning

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[8]-[10]. It is also reported that increasing the nitrogen level actually reduces the risk of nitride formation. This may appear contradictory, but is due to an increase in austenite content and so a reduction in the distance between austenite islands.

Fig. 3 shows microstructures of the ingots observed by optical microscopy. Duplex microstructures are observed in the ingots without nitrogen (No. 1 and No. 3) as shown in Fig. 3 (a) and (c), but are totally different from those of N-containing ingots (No. 2 and No. 4), as expected from phase equilibrium calculation given in Fig. 2. Bright phase in Fig. 3 (a) is austenite (γ) and dark one ferrite (α), of which the fraction is measured as about 0.2. On the other hand, the microstructure of the ingots containing nitrogen in Figs. 3 (c) and (d) shows nearly austenitic single phase and precipitates along grain boundaries. Precipitates were determined as carbo-nitrides. Phase fraction of ferrite measured was very low comparing with thermodynamic calculation given in Fig. 2, which is because the kinetics is not considered in the thermodynamic calculation.
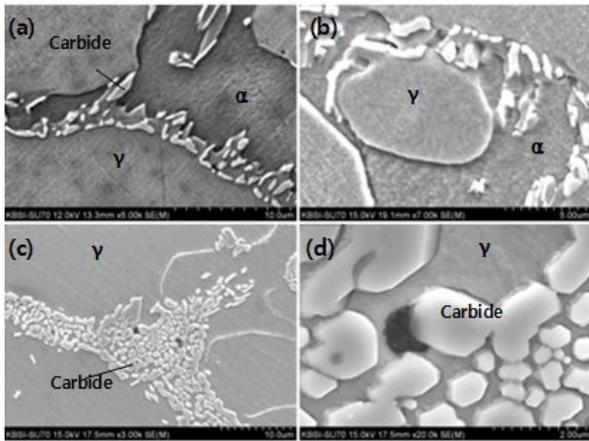
Fig. 4 Back scattered SEM images of the ingots No. 1 (a, b) and No. 2 (c, d)

Fig. 4 shows scanning electron micrographs showing constituent phases of ingots No. 1 and No. 2, obtained by back scattered electron mode. In both ingots, a lot of carbides particles can be observed along the grain or phase boundaries. In the case of the ingot with nitrogen (No. 2), typical appearance of eutectic carbide (Fig. 4 (c)) is apparent. It is very interesting to note that island type austenite phase has been observed with carbide particles distributed near the interfaces. The addition of C and N strengthens both ferrite and austenite by dissolving at interstitial sites in the solid solution. And yet, as carbon is undesirable in stainless steel, due to the risk of sensitization, the addition of nitrogen is preferred. Further, as nitrogen is a strong austenite stabilizer its addition to duplex stainless steel suppresses austenite dissolution and encourages austenite reformation in the heat affected zone (HAZ) in a weldment [10].

Fig. 5 shows tensile and compression tests results conducted at 1230°C on the ingots. Strengths of duplex stainless steels are much higher than that of 310S stainless steel. The highest strength was obtained in the ingot No. 4 containing both N and Y. It is very interesting to note that the combinatory addition of

N and Y is very effective in increasing the high temperature strength. The high strength of the ingot No. 4 was attributed to the fine precipitates expected to form from high temperature above 1200°C, which are found to be very fine and stable as shown in Fig. 6. The fine and angular precipitates were $M_{23}C_6$ type carbides.
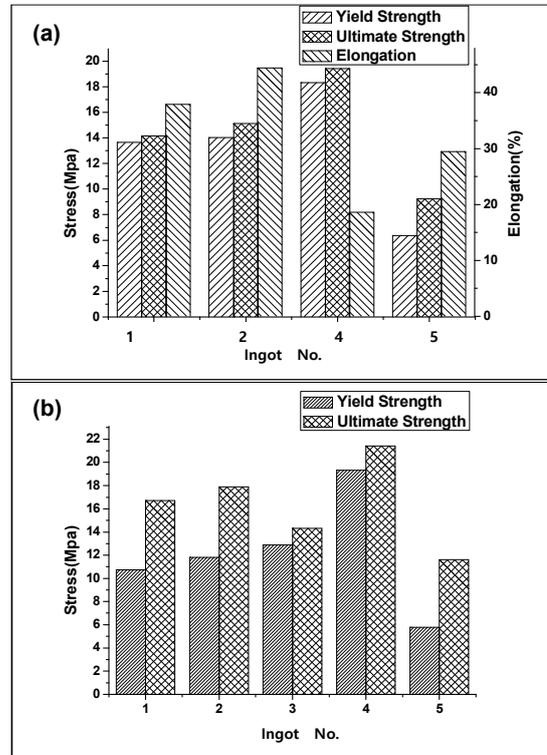
Fig. 5 Tensile (a) and compression (b) tests results obtained at temperature of 1230°C
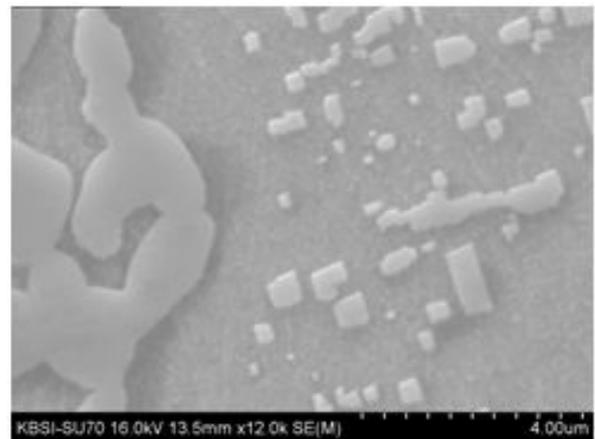
Fig. 6 Morphologies of carbides formed in the ingot No. 4 during solidification and hot exposure

Fig. 7 shows hardness test results obtained from the ingots after hot exposure at 1230°C for up to 200 hrs. For comparison, hardness's of as-cast ingot before hot exposure were also given and labeled "as-cast" in the figure. Hardness of the ingot fabricated in this study is much higher than that of 310S stainless steel (No. 5) and increased with the addition of N and

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Y. It is also noted that hot exposure at 1230°C up to 200 hrs has no prominent effect on the hardness of duplex stainless steels. From the experiments of hot exposure of the ingots at 1230°C up to 200 hrs to examine the stability of microstructure, with annealing time increased up to 200 hrs, it was apparent that duplex phase structure (Fig. 5 (a)) of the ingot No. 1 became single phase structure of austenite after 64 hrs. Dissolution and reprecipitation of carbides were also observed in both ingots. In the early stage of hot exposure, dissolution of carbides occurred and followed by reprecipitation and spheroidization after 16 hrs. Reprecipitation of carbides occurred not only along the interfaces but also in the grain matrices, which increased hardness of duplex stainless ingots as shown in Fig. 7. It is obvious that hot exposure 1230°C increase the hardness although the extent is small and this is caused by reprecipitation of carbides.
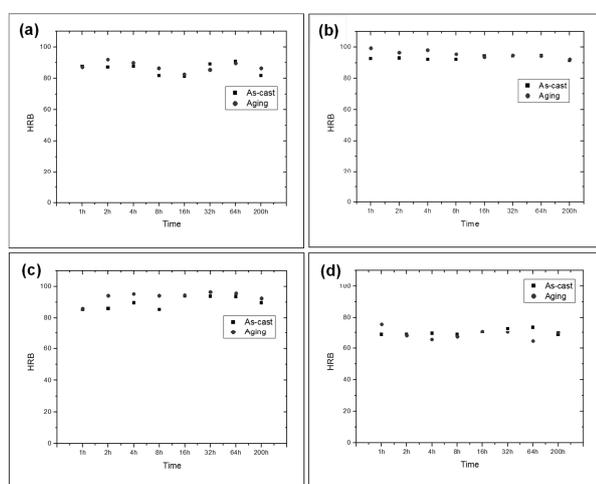
Fig. 7 Hardness as a function of annealing time in the hot exposure conducted at 1230°C on the ingot No. 1 (a), No. 2 (b), No. 4 (c) and No. 5 (d)

IV. CONCLUSIONS

Duplex stainless ingots were cast and evaluated to attempt application to the retort for production of Mg reduction, where both high temperature strength and hot workability are required at the same time. Microstructure observation, hot exposure, high temperature tensile and compression tests and hardness test were carried out. Thermodynamic calculation for stable phases and their fractions revealed that main constituent phases are FCC austenite and BCC ferrite and that the carbides can occur from the liquid phase. Duplex microstructure was observed in the ingot without nitrogen, austenite (γ) and ferrite (α), and the fraction of ferrite was about 0.2. On the other hand, the microstructure of the ingot with nitrogen showed nearly austenitic single phase and precipitates along grain boundaries. With exposure at 1230°C, duplex phase structure became single phase structure of austenite and dissolution and reprecipitation of carbides were also observed. Reprecipitation of carbides occurred both at interfaces and in the matrices, which increased hardness of duplex stainless steels.

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