Materials & Design 83 (2015) 820–828

Contents lists available at ScienceDirect

Materials & Design

journal homepage: www.elsevier.com/locate/matdes

Investigation on the solution treated behavior of economical 19Cr duplex stainless steels by Mn addition

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ARTICLE INFO

Article history:
Received 11 November 2014
Revised 18 May 2015
Accepted 23 May 2015
Available online 20 June 2015

Keywords:
Duplex stainless steels
Mn addition
Solution treatment
Toughness
Pitting corrosion

ABSTRACT

Effect of Mn on microstructure, mechanical property and pitting corrosion of 19% Cr economical duplex stainless steels with solution temperatures ranging from 1040 to1220 °C has been investigated. The austenite content increases with more Mn addition, but decreases by increasing solution temperature, which can be inferred by trend of partition coefficient K_{Mn} with solution temperature. Meanwhile, a balanced austenite-ferrite duplex structure of solution-treated specimens was obtained with Mn addition. The impact energy at 20 °C increased with decreasing solution temperature from 1220 °C to 1040 and 1120 °C, and improved by more Mn addition due to more ductile austenite phase formation. These toughness variations were consistent with fracture morphology characteristic changing. The effect of more Mn addition and solution treatment of 1120°Con decreasing of tensile strength and 0.2% offset yield strength were slight. However, the elongation to fracture (%) fell greatly with Mn addition up to 8.1 wt.% for as-rolled and solution treated specimens due to larger deformation strains of austenite than that of ferrite. The decreasing trend of pitting corrosion potential became slower with Mn addition from 3.6 to 8.1 wt.%. The pitting corrosion resistance was lowered by increasing solution temperature due to more weakened repassivation ferrite phase formation.

1. Introduction

Duplex stainless steels (DSS) exhibit an attractive combination of mechanical properties and corrosion resistance and are thus widely used in various applications such as power plants, desalination facilities, the marine industry, and chemical plants [1–3]. It is well known that such good properties of duplex steels rely on a two-phase microstructure comprised of approximately equal amounts of austenite (γ) and ferrite (δ) [4]. Solution treatment is important heat treatment process for DSS, which can promote dissolution of carbide and other precipitation phases after rolling process, thus maintain high mechanical property and corrosion resistance of DSS [5–7]. However, different solution treatment temperatures can result in volumetric equilibrium fraction of δ and γ phase changes in DSS, and Cr, Mn and Mo content in the two phases will be altered accordingly. These changes have a great influence on ferrite phase transformation behavior and mechanical, corrosion and formability [8].

Li et al. [9] reported that both the ferrite content and the decomposition dynamics in ferrite caused by solution treatment affect the followed thermal aging behavior. Solution treatment is an important process in the production of DSS. It is generally used to re-dissolve the harmful precipitates and eliminate the macro-segregation. In addition, the content, shape and distribution of the ferrite phases, as well as the alloy compositions in ferrite and austenite, can be adjusted by altering the solution temperature and time. The decomposition kinetics in ferrite is closely related to the chemical compositions, especially the Ni content, which could be changed in the solution treatment process.

It is known that nitrogen can improve the pitting corrosion resistance as well as enhance the strength of stainless steels [10]. Meanwhile, the manganese has been considered for austenite former and added to increase solubility of nitrogen in stainless steels [11–13], and its detrimental effect on the pitting corrosion resistance is usually associated with MnS inclusion formation. Besides that, Toor reported that the resistance to pitting and metastable pitting corrosion of a new high Mn–Ni free DSS decreased with increasing Mn content since the number of (Mn, Cr) oxides acted as preferential sites of pitting [14].

In addition to commonly used austenite stabilizing element Ni, the Mn, C, and N elements also can be used as substitutions for Ni additions to stabilize the austenitic structure effectively [15,16], but the good welding performance require low carbon content for DSS application. Nitrogen, as an austenite stabilizer, also

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http://dx.doi.org/10.1016/j.matdes.2015.05.052
0264-1275/

improves resistance and increases strengthening effect of steel [17,18], while its limited solubility in stainless steel increase production difficulty of DSS. Manganese is approximately 5–8 times cheaper than Ni, and is an effective austenitic stabilizer with increasing solubility of nitrogen in stainless steels. Thus, the Mn–N duplex stainless steels are actively being developed by replacing expensive Ni with low cost Mn with a certain amount of nitrogen addition. Jang et al. believed that tensile properties of CD4MCU cast duplex stainless steel was determined by the volume fraction of hard ferritic phase and the shape of austenitic phase, and the resistance to pitting corrosion and stress corrosion cracking in 3.5% NaCl + 5% H_2SO_4 aqueous solution was recovered with the addition of 0.8% Mn to 2% Mn [19]. However, the effect of Mn on the microstructural evolution, as well as the mechanical and corrosion properties, of duplex stainless steels has not been well established.

On the other hand, solution treatment is an effective way to maintain the high resistance to localised corrosion, by which the alloying elements can be in solid solution and homogeneously distributed in metal in order to attain passivation effect. Thermal aging behavior of DSS is closely related to the ferrite content and the chemical compositions in ferrite. For a particular grade of steel, these factors are controlled by the fabrication process, including the solidification and the following heat treatment, especially by the solution treatment process.

However, little information exists regarding the influence of Mn on the mechanical property and pitting corrosion of DSS under different solution treatment temperatures. Therefore, the present work attempts to provide a further understanding of the effect of Mn additions on microstructure, mechanical property and pitting corrosion resistance of 19% Cr economical duplex stainless steel under different solution temperatures.

2. Experimental procedures

The raw materials were melted in a 25 kg vacuum induction furnace then cast as a single square ingot. The casting ingots were hot forged into 30-mm plates, then the as-forged samples were hot rolled into 12 mm plates at temperature ranging from 1050 to 1200 °C. The chemical compositions of the rolling plates, designated as Alloy 1, Alloy 2 and Alloy 3, are shown in Table 1. Samples with dimension of 12 × 12 × 50 mm were cut from these rolling plates then solution treated at 1040 °C, 1120 °C, 1220 °C for 30 min respectively, followed by water quenching. The microstructures of specimens were electrochemically etched by 40 wt.% KOH solution for optical microscopy observation. Tensile tests were performed at room temperature with specimens having a gage length of 25 mm and diameter of 5 mm according to the National Standard of the P.R.C., GB/T228-2002, the specimen gage section was oriented parallel to the rolling direction. Charpy impact tests were performed at 20 °C, and the direction of the V-notch was oriented perpendicular to the rolling direction.

The volume fractions of austenite phase were measured using the method of manual point count according to ASTM E 562 as follows [20]: the magnification of the micrograph was 500 × and the grid size (number of points) was 20. Any point that fell on the phase studied was counted as one, otherwise zero. In addition, the point fell on the boundary was counted as a half. Electrochemical potentiodynamic polarization was performed in a deaerated 3.5 wt.% NaCl solution at temperatures varying from 25 °C (±1 °C). A platinum sheet and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. The specimens, embedded in epoxy resin with an exposure area of 100 mm^2, acted as a working electrode. Prior to each experiment, the specimens were ground mechanically up to 3000 grit, rinsed with distilled water and dried in hot air. Anodic potentiodynamic polarization was tested through linear sweep technique at a sweep rate of 0.1 mV/s, from the free corrosion potential to 1200 mV (SCE). All potentials are given against the SCE. After that, the corrosion morphology was observed by SEM. Corrosion potential (E_{corr}), passive film breakdown potential (E_b), passivation current density (I_p) were obtained from the polarization curves. Corrosion current density (i_{corr}) is commonly obtained by the extrapolation of the cathodic and anodic slopes between 50 and 100 mV away from Ecorr. Eb is the potential the passive film breaks down then leading to rapid increase of current density and it was determined as the current density reached a value of 100 $\mu A/cm^2$.

3. Results and discussion

3.1. Microstructure and composition analysis

Fig. 1 shows optical microstructures obtained from the specimens with different Mn contents after solution treatment at 1040 °C, 1120 °C and 1220 °C. Under such conditions, they show an obvious duplex structure of austenite and ferrite. The bright etched austenite (γ) islands were embedded in a gray etched ferrite (δ) matrix, and no obvious secondary precipitates were found in the ferrite, austenite matrix and γ/δ phase boundaries. The microstructures of different Mn content specimens varied significantly with different solution treatment temperatures from 1040 to 1220 °C. The volume fraction as a function of solution treatment temperature is plotted in Fig. 2 for the specimens solution treated at different temperatures. With an increase in Mn content from 3.6 to 8.1 wt.%, the amount of austenite phases increased, which was reduced greatly by increasing solution treatment temperature from 1040 to 1220 °C. Under these three different solution treatment temperatures, the volume fractions of austenite phases ranging from 40.1% to 60.9% were obtained, indicating good balance of duplex phases with different Mn addition. When treated with solution at 1040 °C, the austenite volume of sample alloy 1 was 54.1%, while the austenite volume of samples alloy 1 and alloy 2 was 52.5% and 54.6% respectively with solution treatment at 1120 °C, which has a microstructure consisting of ferrite and austenite phases with approximately a 1:1 ratio. This suggested that low Mn content addition in 19% Cr economical DSS can promote austenite phases formation with comparatively wide solution treatment temperature, which covered a commonly used solution treatment temperature of 1050 °C in DSS production. However, increasing solution treatment temperature to 1220 °C greatly reduced austenite volume fraction, indicating that effect of Mn on austenite formation was reduced by higher solution temperature.

The Cr, Ni equivalent formulas of Schaeffler graph are as follows [21]:

Table 1
The chemical composition of hot rolled 19% Cr duplex stainless steel (wt.%).

Elements	C	Si	Mn	S	P	Cr	Ni	Mo	N	Other
Alloy 1	0.01	0.13	3.59	0.006	0.007	19.34	1.56	0.98	0.21	Bal.
Alloy 2	0.01	0.11	5.54	0.005	0.007	19.43	1.59	0.92	0.22	
Alloy 3	0.01	0.12	8.10	0.005	0.006	19.55	1.55	0.87	0.20	