Effect of the Heat Treatment Parameters on the Phase Transformation and Corrosion Resistance of Fe-14Cr-3Mo Martensitic Stainless Steel

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Carbide dissolution during heating processes can change chemical composition of martensitic stainless steel in its austenitic phase. Although the austenitizing treatments were carried out at a homogeneous austenite region, the amount of carbon atom in the matrix differs. Increase in the amount of carbon contents in the matrix resulted in decreasing MS temperature, which consequently causes the volume fraction of the retained austenite to increase. This study reveals the effects of the austenitizing treatment on the properties of Fe - 0.3C - 14Cr - 3Mo martensitic stainless steel change with different austenitizing temperatures.

Keywords : *stainless steels, martensite, phase transformation, corrosion resistance, carbides, retained austenite, heat treatment parameters*

1. Introduction

Martensitic stainless steel is commonly used to manufacture components with high strength and moderate corrosion resistance. Special heat treatments make the steel suitable for a wide range of applications such as steam generators, pressure vessels, cutting tools, and offshore platforms for oil extraction.[1] Because of a relatively complicated structure, the steel requires careful heat treatment to ensure a fully martensitic structure, to avoid δ-ferrite formation and to ensure transformation into martensite rather than into ferrite during cooling stage.

Martensitic steels are used normally in an austenitized and tempered condition.[2] This heat treatment involves a solutionizing treatment (austenitizing) that produces austenite and dissolves carbides. After the heat treatment, the material is cooled in air to transform of austenite to martensite.

Often consisting of martensite phase, undissolved and reprecipitated carbides, and δ-ferrite, the microstructure of martensitic steel changes depending on its composition and processing history. The strength and corrosion resistance of the material depend on the degree of the dissolution of carbides. Although austenitizing temperature is higher than the upper critical temperature of A_{CC}, the alloy needs to be heat-treated at an even higher temperature for complete dissolution of chromium carbides. Factors, such as grain coarsening, austenite retention, and δ-ferrite formation in the quenched microstructure, should be considered in selecting a suitable austenitizing temperature.[3]

In martensitic stainless steels, carbide dissolution processes alter the chemical composition of the austenitic phase during heating. Consequently, the heating parameters have a significant effect on the transformation behavior of the austenite phase during continuous cooling. During the heating treatment, carbide dissolution can change chemical composition of martensitic stainless steel at the austenitic phase.[4] Heating parameters play critical roles in the transformation into the austenite phase. Although the austenitizing treatments were carried out at the homogeneous austenite regions, the amount of carbon atoms in the matrix differs. The reason is that carbide dissolution and M_S temperature of the alloy are affected by the Andrew's equation (MS (℃) = 539 - 423 × wt% C - 30.4 × wt% Mn - 12.1 × wt% Cr - 17.7 × wt% Ni - 7.5 × wt% Mo + 10 × wt% Co - 7.5 × wt% Si). Increase in the amount of carbon contents in the matrix resulted in decreasing M_S temperature, which consequently causes the volume fraction of the retained austenite to increase.

This study investigates the effects of austenitizing temperature and heat treatment parameters of Fe - 14Cr - 3Mo martensitic stainless steel on corrosion resistance

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and phase transformation in relation to the dissolution and reprecipitation of carbides.

2. Experimental procedures

In this study, the chemical composition of the investigated alloy is Fe-0.3C-14Cr-3Mo-1.5Ni-0.12N in wt%. which is manufactured through vacuum induction melting. Conditions of austenitizing treatment are heating at 1000, 1050, and 1100 ℃, and then air cooling. The hardness was measured on the C-scale using a Rockwell hardness tester with the load maintained at 150 kg. Ten measurements were conducted to produce a mean value excluding the maximum and minimum.

The microstructural characteristics of the heat-treated specimens were examined with an analytical microscope. Transmission electron microscope was also used to characterize only the carbides isolated from the matrix. Electron backscatter diffraction (EBSD) analysis provided information that would normally require transmission electron microscopy, without the associated difficulties of sample preparation and small sample size. The X-ray diffraction tests were performed with the Cu target (wavelength of 1.5406 Å) and the volume fraction of the retained austenite was determined by ASTM E975.

Potentiodynamic anodic polarization tests were performed to characterize the electrochemical behaviors of the samples in 3.5 wt% NaCl solution at 25 ℃. The effect of the retained austenite was evaluated through the specimens cooled at the temperature down to -196 ℃ by using liquid nitrogen (LN), "Sub-zero treatment."

3. Results and discussions

3.1 Changes in hardness with austenitizing temperatures

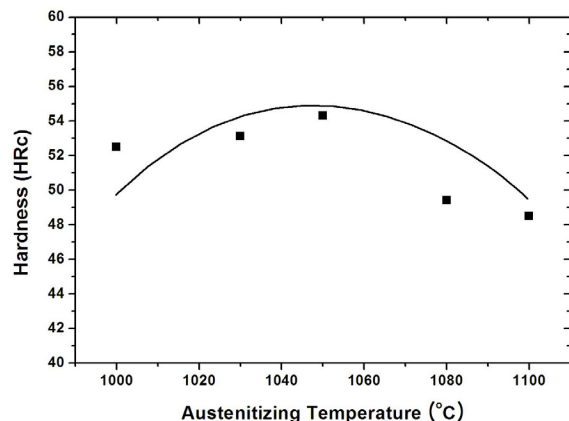Fig. 1 shows changes in hardness with austenitizing

Fig. 1. Variation of hardness with austenitizing temperature

temperature. It is possible to assume the phases which can be produced in the heat treatment process by hardness changes. As the temperature rose, the hardness value increased to some degree, which is resulted from the increased amount of carbon in the matrix due to the dissolution of the carbides. However, hardness moved in the opposite direction to the austenitizing temperature. It was weakened as the austenitizing temperature went up. This was attributed to the untransformed austenite phase during the quenching process.

3.2 Imaging

Fig. 2 shows the altering distribution of $M_{23}C_6$ (Cr-rich) at different austenitizing temperatures through carbon extraction methods. It is possible to expect that the types of the carbide which forms in high temperature in this alloy are $M_{23}C_6$ (Cr-rich).[5] And the approximate composition of the carbides is shown in Fig. 2 (d). This indicates that the carbide particles are enriched in elements mainly such as Cr, Mo, and Fe. It is possible to assume that that the enrichment of these elements in the precipitated carbides deteriorates the corrosion resistance of the matrix because Cr-depleted zone is formed.

The EBSD patterns of the experimental alloy observed at each austenitizing temperature are presented in Fig. 3. The specimen was tilted about 5 degrees to find out Kikuchi patterns. It is difficult to identify the prior austenite grain and distinguish the retained austenite from the matrix in the optical microscopy. However, the results of EBSD analysis provide the phase difference between the martensite phase (α') and the retained austenite (ɤ). The fraction of the retained austenite is largely observed at different austenitizing temperatures because the dissolution of the precipitated carbides will lead the enrichment of the solute elements in the matrix and lower the M_S temperature.

3.3 X-ray diffraction

Fig. 4 (a) shows the results of X-ray diffraction tests for the phase analysis after heat treatment. In this study, the wave length of 1.5406 Å using Cu target is used. Fig. 4 (b) shows the fraction of the retained austenite obtained through XRD using ASMT E 975 - 03 and through EBSD analysis. The peaks of Cr-rich $M_{23}C_6$ and α' peak were observed at low temperatures. However, it is not possible to identify martensite and ferrite phases because the axial ratio of the two phases is so close to unity that the peak cannot be detected separately. The peak of the retained austenite as well as α' peak were found when the temperature was elevated.

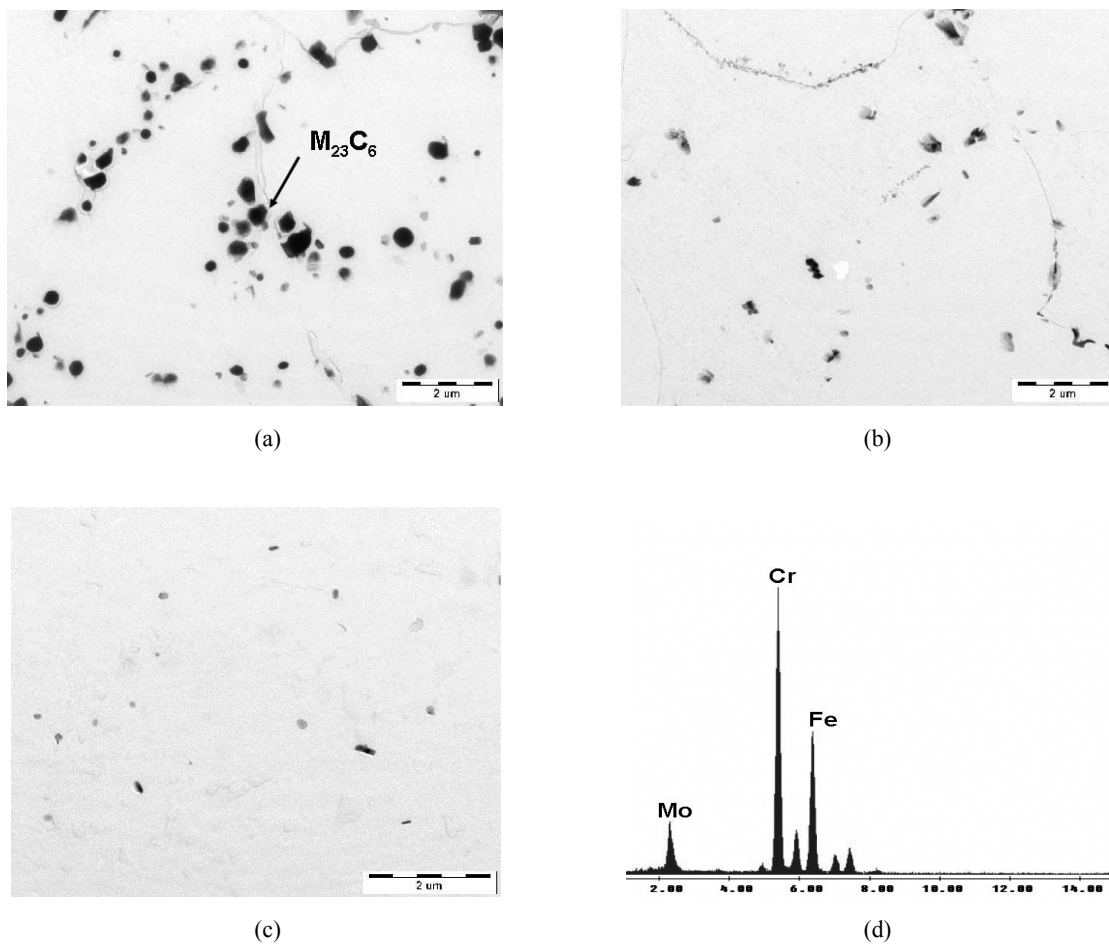This can be explained from the decreased ferrite number

Fig. 2. Effect of austenitizing temperature on the carbide distribution: (a) 1000℃, (b) 1050℃, (c) 1100℃, and (d) EDS analysis of the carbides
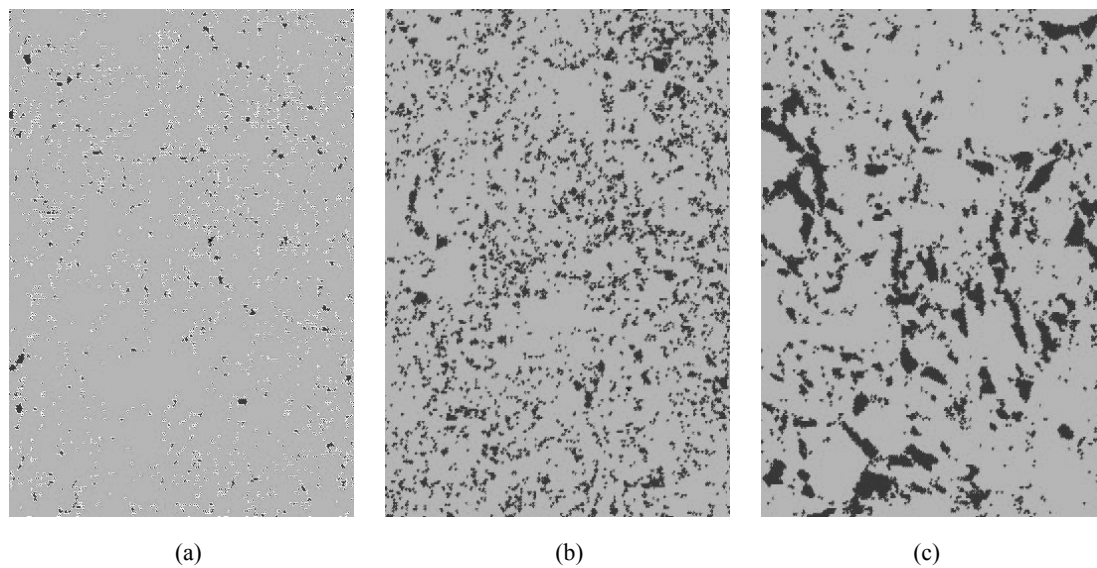

Fig. 3. EBSD patterns of the experimental alloy: (a) 1000℃, (b) 1050℃, and (c) 1100℃
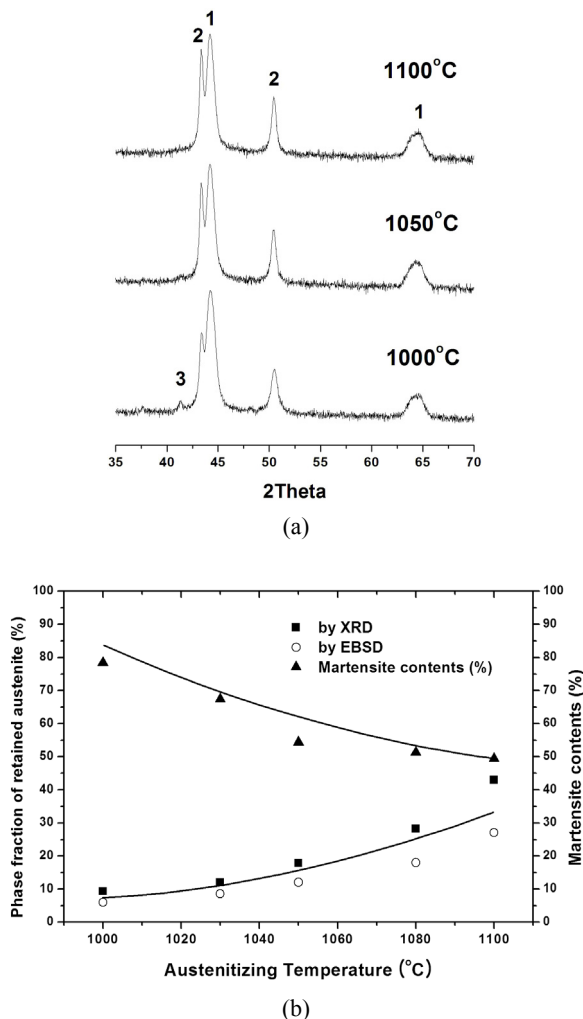
(a)

(b)

Fig. 4. (a) X-ray diffraction patterns according to the austenitizing temperatures: 1; α', 2; γ, and 3; $M_{23}C_6$ (b) Phase fraction of the retained austenite using XRD and EBSD
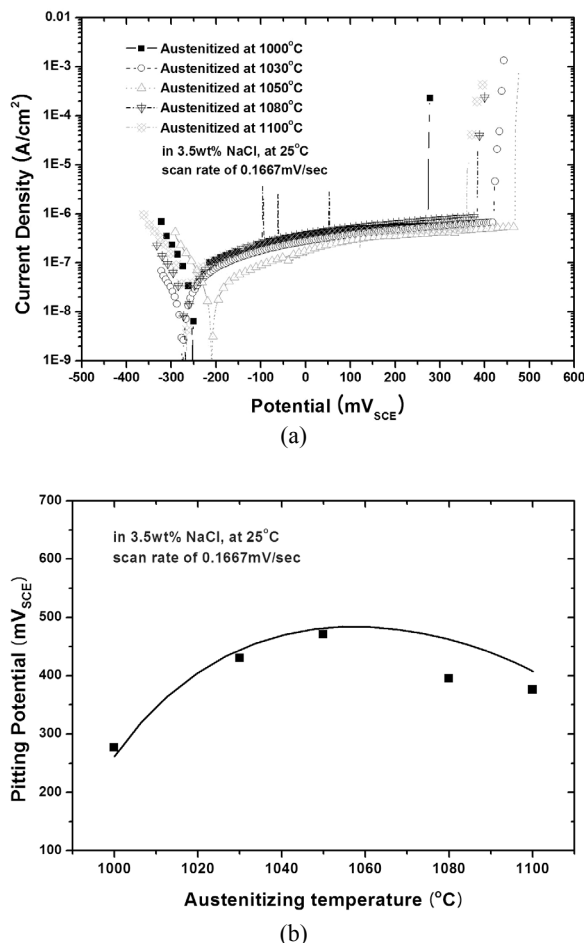

(a)

(b)

Fig. 5. Potentiodynamic anodic polarization test in 3.5 wt% NaCl solution: (a) anodic polarization behavior and (b) E_{PIT} value as a function of the austenitizing temperature

at each heat treatment temperature. The amount of the retained austenite increases because the volume of the carbon atom in the matrix increases with the carbides dissolved. And the pinning of clustered vacancies to the partial dislocations hinders the nucleation of martensite and consequently depresses the M_S temperature.[6] This phase distribution can be used to decide the degree of the corrosion resistance, because the existence of Cr-carbides creates Cr-depleted zone, and the retained austenite impairs the balance of corrosion resistance in the matrix (mainly α').

3.4 Potentiodynamic anodic polarization test

Fig. 5 shows the results of potentiodynamic anodic polarization tests in 3.5 wt% NaCl solution at 25 ℃. Passive regions where the current densities are ranged at 1~3 μA/cm² are displayed. The pitting potentials (E_{PIT}),

which are the breakdown potential for passivation and the potential for 100 μA/cm² current density of the experimental alloy, are 270 mV_{SCE} at 1000 ℃, 470 mV_{SCE} at 1050 ℃, and 376 mV_{SCE} at 1100 ℃ as presented in Fig. 5 (b). The highest value of the E_{PIT} appeared when the alloy was austenitized at 1050 ℃. This phenomenon can be explained by the reduced corrosion resistance to the chloride ions. Cr-depleted zone is known to deteriorate corrosion resistance due to the undissolved carbides within the matrix and the differences in corrosion resistance.

A. F. Candelaria demonstrated[7] that there must be another mechanism controlling the corrosion resistance that superimposes the beneficial aspect of the carbide dissolution. This behavior must be explained as a consequence of the increase of the internal martensite lattice stresses promoted by the increase of the carbon saturation when the austenitizing temperature is raised. As the volume fraction of retained austenite increases the internal stresses decrease promoting a beneficial influence on

corrosion.

3.5 Sub-zero treatment

Thermal stability of the retained austenite is created by lowering M_S temperature below the room temperature and increasing carbon contents in the matrix. The effect of the retained austenite was evaluated through the specimens cooled at the temperature down to -196 ℃ by using liquid nitrogen (LN), "Sub-zero treatment." Sub-zero treatment results in some transformation of retained austenite to martensite.

The results of X-ray diffraction patterns and the phase fraction are shown in Fig. 6 (a). The fraction of the retained austenite decreased especially austenitized above 1050 ℃ after sub-zero treatment. This stability of the austenite particle is probably due to the increased difficulty in propagating the shear of the martensitic transformation via the increased barriers afforded by the substructure in the austenite particles.[8] Fig. 6 (b) shows the anodic
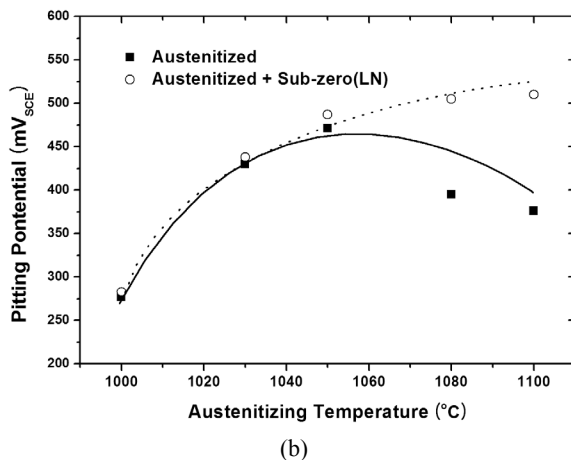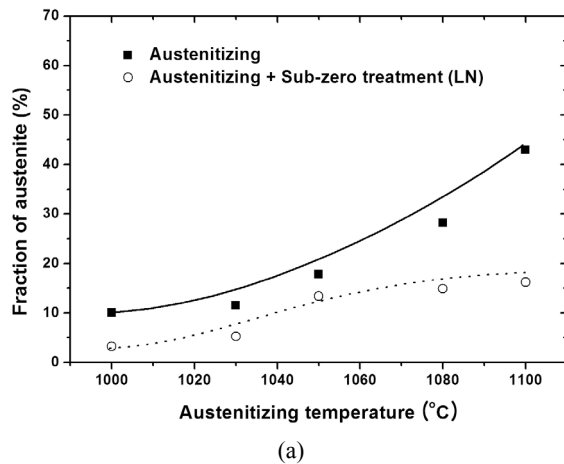

(a)

(b)

Fig. 6. (a) phase fraction after sub-zero treatment in the liquid nitrogen, and (b) comparison of the E_{PIT}

polarization test results obtained before and after the sub-zero treatment in 3.5 wt% NaCl solution. After the sub-zero treatment, the E_{PIT} values of high austenitizing temperatures do not decrease as before treatment. The pitting resistance is enhanced by the fact decreasing the austenite fraction which can impair the corrosion balance in the matrix.

4. Conclusions

(1) As austenitizing temperatures increase, the amount of undissolved carbides decreases and the amount of retained austenite generally produced at high temperatures increases. The dissolution of carbides raises the volume of carbon content in martensite matrix, which results in the increase in hardness of martensite with increasing austenitizing temperatures.

(2) The fraction of the retained austenite increases according to the austenitizing temperatures because the dissolution of the precipitated carbides will lead the enrichment of the austenite stabilizers as carbon in the matrix.

(3) It is indicated that the different levels of corrosion resistance can be explained by the phase transformation. It is also evident that corrosion resistance is not improved at high temperatures which make carbides totally dissolved into the matrix. The corrosion resistance has not been improved due to the impaired balance of corrosion resistance.

(4) The austenite phase did not transform into martensite and retained their thermal stability even after cooling to -196 ℃ in the liquid nitrogen. This stability of the austenite particle is probably due to increased difficulty in propagating the shear of the martensitic transformation via the increased barriers afforded by the substructure in the austenite particles.

(5) The pitting resistance is enhanced by the fact decreasing the austenite fraction which can impair the corrosion balance in the matrix.

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