Effect of the Cooling Rates on the Corrosion Resistance and Phase Transformation of 14Cr-3Mo Martensitic Stainless Steel

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Martensitic stainless steel is used when mechanical properties such as high tensile strength and hardness are required. Medium carbon-contained martensitic stainless steel which contains more than 0.2 wt% of carbon should be heat-treated and quenched at the temperature where undissolved carbides are totally dissolved into the matrix. In particular, the dissolution and reprecipitation behaviors of various forms of carbides are affected by such parameters as heating rate, heating temperature, duration time and cooling rate. This study is to investigate the effects of heat treatment parameters of 14Cr-3Mo martensitic stainless on corrosion resistance and phase transformation in relation to the dissolution and reprecipitation of carbides.

Keywords : *heat treatment parameter; martensitic stainless steel; carbides; corrosion resistance; phase transformation*

1. Introduction

Martensitic stainless steels are commonly used for manufacturing components with high mechanical properties and moderate corrosion resistance, operating under conditions of either high or low temperature. As their properties can be changed by the heat treatment, these steels are suitable for a wide range of applications such as steam generators, pressure vessels, cutting tools, and offshore platforms for oil extraction.[1] These steels are complicated structurally, requiring careful control of heat treatment to ensure a fully martensitic structure.[2]

In martensitic stainless steels,[3] carbide dissolution processes can change the chemical composition of austenitic phase during heating. Consequently, heating parameters will do critical roles in the transformation of the austenite phase. Similarly, the cooling rate influences considerably the austenitic decomposition and transformation in the austenitizing process. The quenching treatment involves annealing to obtain austenite and to dissolve the carbides, followed by cooling to transform the austenite into martensite and, often, to cause carbide precipitation. It is well known that the properties obtained in these steels are strongly influenced by such heat treatments. The amount of carbides in the quenched microstructures exerts an important influence on the characteristics of these ma-

terials. Therefore, the effects of the quenching parameters on the final microstructures have been previously evaluated.[4]

In this study, it is investigated that the effects of heat treatment parameters of 14Cr-3Mo martensitic stainless on corrosion resistance and phase transformation in relation to the dissolution and reprecipitation of carbides.

2. Experimental procedures

The chemical composition of the investigated alloy is 0.3C-14Cr-3Mo-1.5Ni-0.12N. To investigate the effects of the parameters such as heating temperature and cooling rate on phase transformation, temperature is maintained at 1000 and 1050°C above A_{C3} temperature for five minutes respectively and cooled at the rates of 0.5°C/s, 1.0°C/s, 2.0°C/s and 10°C/s to room temperature. Transmission electron microscope was used to observe only the carbides isolated from the matrix. The carbon extraction replicas for the precipitation analysis were prepared from the specimen that had been polished through 1 μm diamond suspension. Potentiodynamic anodic polarization tests were performed to characterize the electrochemical behaviors of the samples in 3.5 wt% NaCl solution at 2 5°C. The working electrode was reduced potentiostatically at -750 mV$_{SCE}$ for 10 min, and then maintained at open circuit potentials (OCP) for 10 mins. After maintaining at OCP, the potential scan (1mV$_{SCE}$/s) was carried out from

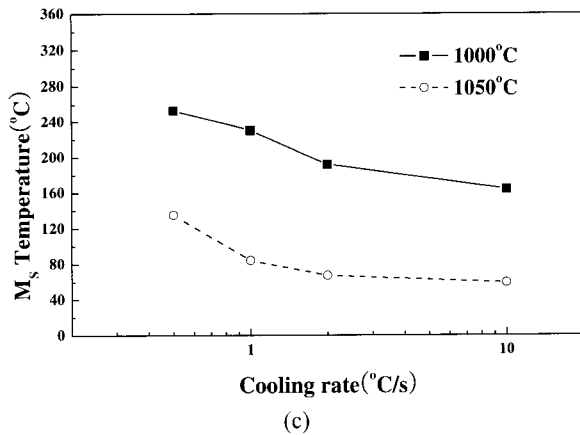†Corresponding author: yongsoop@yonsei.ac.kr

(a)

(b)

(c)
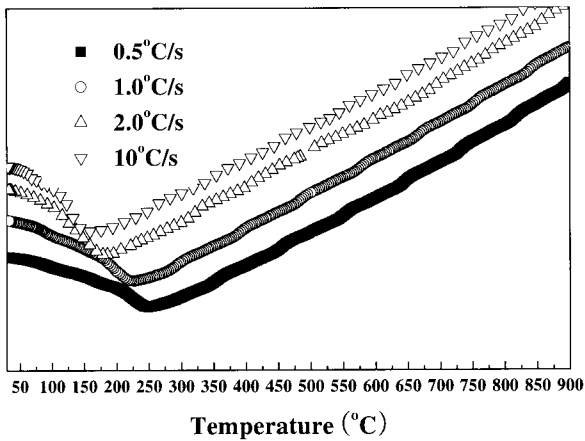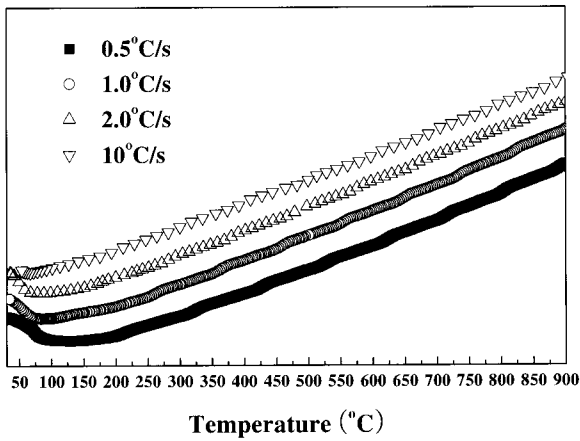
Fig. 1. The dilatometric curves for the specimen austenitized at (a) 1000°C, (b) 1050°C, and (c) Ms temperatures measured from dilatometric curves

-250 mV$_{SCE}$ of OCP to 800 mV$_{SCE}$.

3. Results and discussion

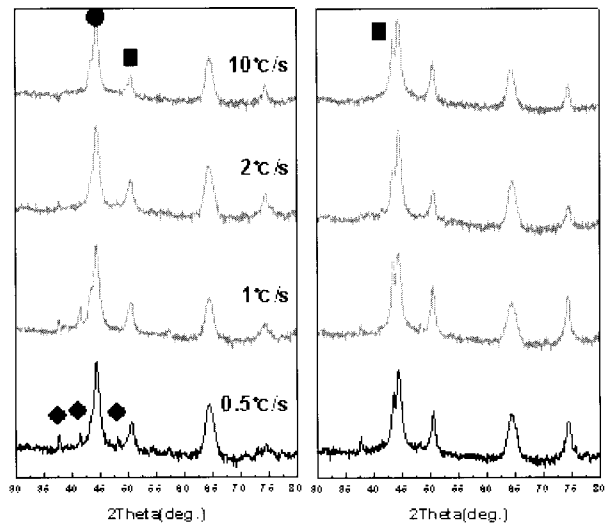Fig. 1 (a) and (b) show the dilatometric curves for the

Fig. 2. X-ray diffraction patterns of the experimental alloy according to the austenitizing temperatures and cooling rates(● : α', ■ : retained austenite, and ◆ : $M_{23}C_6$)

specimen austenitized at 1000°C and 1050°C for 5 min and followed by the cooling at different rates (0.5-10°C/s). It was observed that Ms temperature decreased with increasing austenitizing temperature and cooling rate. And Fig. 1 (c) shows the Ms temperature measured from different dilatometric conditions. These results indicate that higher austenitizing temperatures with the higher cooling rates depressed the martensitic transformation. Carbon atom has more powerful solid-solution streng-thening effect on austenite than the other alloying elements; it was judged that the element in steels influences the Ms temperature the most. And if the strength of the prior austenite were improved due to the increase in carbon content, Ms temperature would be lowered.[5),6)]

In Fig. 2, the result of X-ray diffraction tests for phase identification is shown. At a lower austenitizing temperature, the peaks of Cr-rich $M_{23}C_6$ and α' peak were observed. 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.[7)] The peak of retained austenite as well as α' peak was found, which is due to the increase of carbon in the matrix. The amount of the retained austenite phase increases according to the cooling rate at the same austenitizing temperature and vice versa. The increase is caused by the larger amount of carbon atom in the matrix from the dissolution of the carbides, and the pinning of clustered vacancies to the partial dislocations hinders the nucleation of martensite and consequently depresses the Ms temperature.[5)]

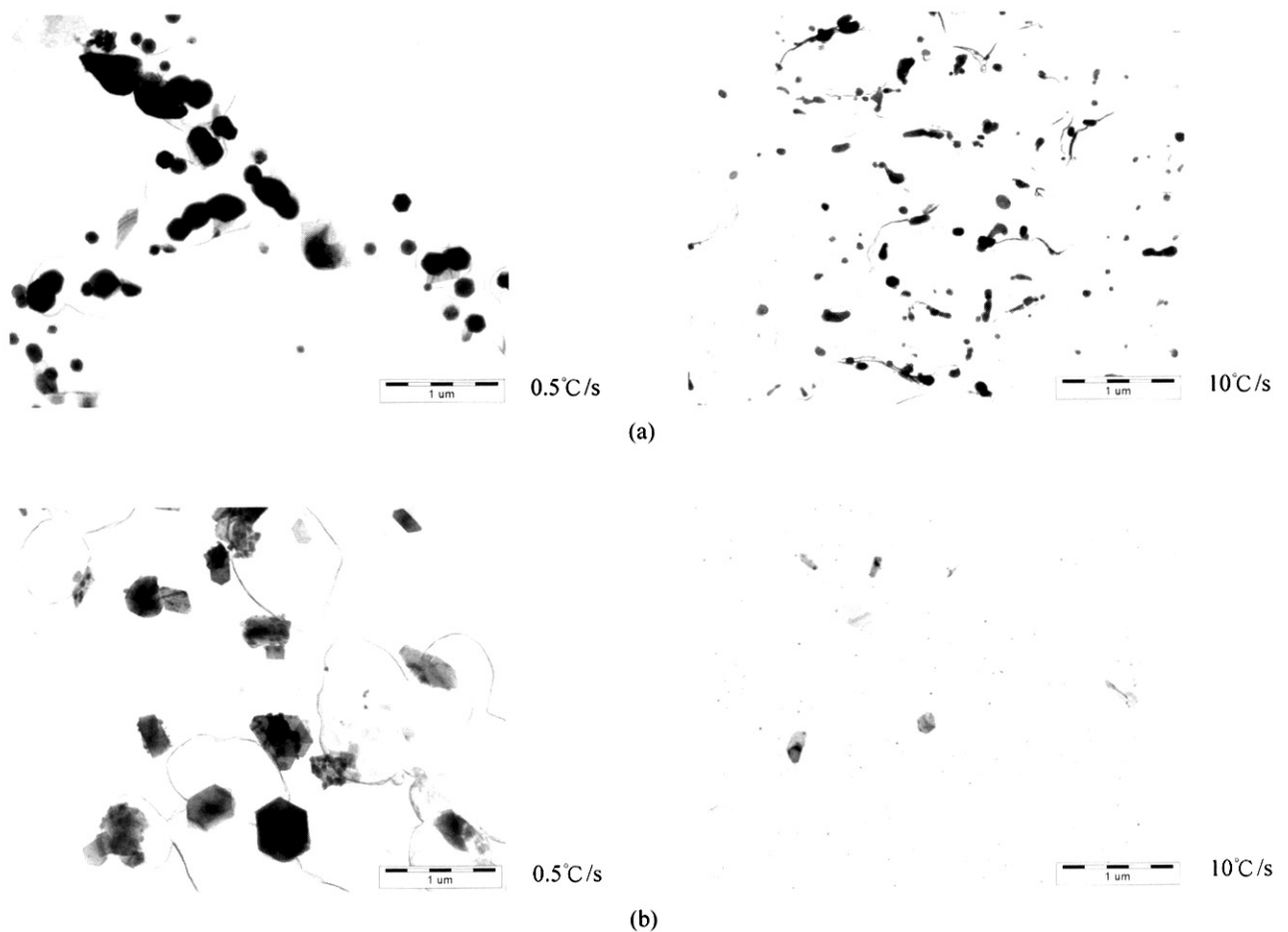Fig. 3 shows the changes in the distribution of $M_{23}C_6$

Fig. 3. Effect of austenitizing temperature and cooling rates on the carbide distribution of the experimental alloy; (a) 1000℃ and (b) 1050℃

(Cr-rich) with different austenitizing temperatures and cooling rates using carbon extraction methods. The size and morphology of the carbides observed at 1000℃ suggest that they be residual carbides undissolved during austenitizing treatments. Although the austenitizing temperatures are constant, the size and Cr contents of the carbides increase with decreasing cooling rates. However, the amount of carbides decreases as the heating temperature increases. The dissolution of $M_{23}C_6$(Cr-rich) increases the contents of Cr and Mo as well as C acting as an austenite stabilizer, thereby the corrosion resistance was expected to be enhanced.

Fig. 4 shows the corrosion resistance of the experimental alloy according to the changes in the austenitizing temperatures and the cooling rates. Corrosion resistance for pitting has improved as cooling rates increases at the same austenitizing temperature. This is assumed that the undissolved and precipitated carbides formed during the quenching process can deteriorate the corrosion resistance of the specimen in NaCl solution by the formation of

Cr-depleted zone and decreasing Cr and Mo contents in the matrix. However, the corrosion resistance has not been improved at the highest cooling rate due to the impaired balance of the corrosion resistance among the matrix (mainly α') and the retained austenite which is formed during the cooling stage by the depressed martensitic transformation.

4. Conclusions

It is found that at the same cooling rate the specimen austenitized at the higher temperature has a lower martensitic start temperature (Ms). The difference of Ms becomes much larger at the higher cooling rate. This result provides that the higher austenitization temperature with the higher cooling rate depresses the martensitic transformation. These results mentioned above are explained by the Cr-carbides dissolution and increasing carbon concentration in matrix. Corrosion resistance has improved as cooling rates increases. But at the highest cooling rate,
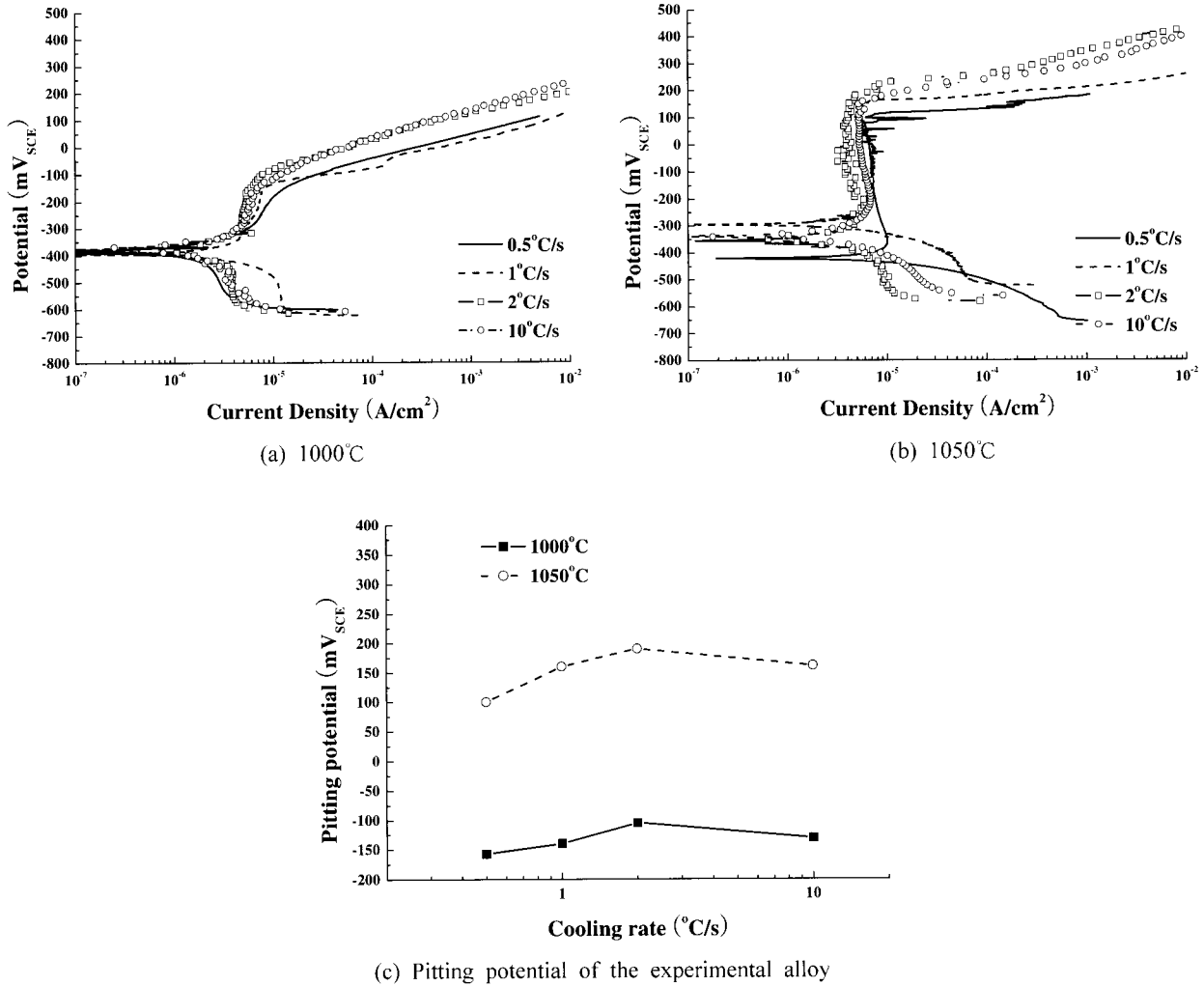
(a) 1000°C

(b) 1050°C

(c) Pitting potential of the experimental alloy

Fig. 4. Potentiodynamic anodic polarization test in 3.5wt% NaCl solution, 25°C (a) Cooled from 1000°C (b) 1050°C, and (c) Pitting potential according to the austenitizing temperatures and cooling rates

it is shown the opposite results due to the impaired balance of corrosion resistance among the matrix (mainly α') and the retained austenite.

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