Electrochemical and Atom Probe Studies of Cast and Aged Duplex Stainless Steel

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Cast duplex stainless steel of CF3M was aged at 450°C for up to 10000 h. The ferritic phase was hardened and embrittled by the ageing. Cyclic polarization curves were measured in 0.5 kmol/m³ H₂SO₄+0.01 kmol/m³ KSCN solution to investigate the electrochemical behaviour during phase decomposition of the ferritic phase. In addition, the 3-D microchemical change was examined by a recently built position sensitive atom probe (POSAP). The reactivation current peak appears in the cyclic polarization measurement after 400 h ageing. This results from the dissolution of the chromium-depleted iron-rich region formed during decomposition of the ferritic phase.

The POSAP analysis of the 10000 h aged steel shows a well-developed phase decomposition into the chromium-rich and iron-rich regions in several nanometer scale. Flat plate-like chromium-rich regions (Cr ≥ 50 at%) of a few nanometer thickness are observed at a spacing of a few nanometer, while the iron-rich regions (Cr < 12 at%) form the percolated structure surrounding the flat plate-like chromium-rich regions.

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I. Introduction

The ferritic phase of cast stainless steels with duplex austenitic-ferritic microstructure is known to undergo phase decomposition when aged at temperatures in the range of 300 to 500°C, resulting in significant hardening and embrittlement⁽¹⁾⁽²⁾. The embrittlement is generally attributed to spinodal decomposition of the ferritic phase into chromium-rich α' and chromium-depleted (iron-rich) α domains. The recent microstructural studies⁽³⁾⁻⁽⁸⁾ using atom probe field ion microscopy (APFIM) have indicated that the ferritic phase of CF3, CF8 and CF8M type stainless steels spinodally decomposes during low temperature ageing. Furthermore the recent position sensitive atom probe (POSAP) analysis has clearly demonstrated the formation of the chromium-rich and chromium depleted domains in 3D highly interconnected structure⁽⁹⁾⁽¹⁰⁾. Because of its high spatial resolution and large number of ions collected from a single tip, the POSAP is a powerful tool for the investigation of the ultrafine-scale decomposition of the ferritic phase and may allow a more accurate quantitative description of the phase decomposition.

Recent electrochemical studies⁽¹¹⁾⁽¹²⁾ have shown that thermal ageing of austenitic/ferritic duplex stainless steel of 25Cr-6Ni-3Mo at 450°C influences the electrochemical behaviour of the ferrite phase. The reactivation current peaks similar to the sensitized type 304 stainless steel were observed during the electrochemical potentiokinetic reactivation measurement in 0.1~0.5 kmol/m³ H₂SO₄+0.01 kmol/m³ KSCN solution. This has been attributed to the formation of the chromium-depleted iron-rich region as evidenced by the atom probe⁽¹¹⁾⁽¹²⁾ and by the Mössbauer effect⁽¹³⁾⁽¹⁴⁾.

In the present study electrochemical measurements and metallographic observations were performed on a low carbon, molybdenum bearing CF series cast duplex stainless steel, CF3M aged at 450°C for up to 10000 h. In addition a detailed POSAP analysis was performed and an attempt was made to relate the microchemical result with the dissolution behaviour of the ferrite phase.

II. Experimental

A low carbon, molybdenum bearing cast duplex stainless steel of CF3M (ferrite content 25%) was aged at 450°C for 400, 4000 and 10000 h. The chemical composition is given in Table 1. The electrodes were prepared by spot-welding a lead onto one side of the sample and mounted them into epoxy resin. The surface of the electrode was abraded to 600 grit silicon carbide paper and polished with 0.05 μ m alumina paste. Electrochemical measurements were carried out in 0.5 kmol/m³ H₂SO₄+0.01 kmol/m³ KSCN solution with a typical three-electrode cell. The solution was deaerated with pure nitrogen gas during the measurement. A platinum sheet (20 mm × 20 mm) was used as the counter electrode and a saturated Ag/AgCl electrode as the reference electrode. Before the measurement, the electrode was cathodically polarized at -600 mV (Ag/AgCl) for 5 min.

The microchemical analysis was performed on the unaged and the 10000 h aged specimen using a recently built

Table 1 Chemical composition of the cast duplex stainless steel.

Element	C	Si	Mn	P	S	Cr	Ni	Mo	Fe	N
CF3M (mass%)	0.018	1.19	0.69	0.012	0.004	19.89	9.98	2.42	Bal	0.025

POSAP. Our POSAP employs the POSAP detector of 75 mm in diameter and the associated electronics supplied from Kindbrisk Ltd. With POSAP analysis, field evaporated atoms are identified by the time-of-flight mass spectrometry and the position of impact determined with a wedge and strip anode type position sensitive detector. Time sequences of the atom map obtained are expanded in the 3-D atom map by estimating the depth of field evaporated atomic layers from the applied voltage and the crystallographic structure of the specimen. Subsequent processing was performed on a graphic software (The Application Visualization System from AVS Inc) linked with the POSAP software modules developed by Kindbrisk Ltd. The POSAP 3-D visualization has been briefly described by Cerezo *et al.*⁽⁹⁾.

Specimens for the POSAP were prepared by electropolishing in a mixture of HCl and HNO₃ at 3V AC. Field ion images were obtained using neon as the imaging gas. The POSAP analysis was performed under a pressure of 10⁻¹⁰ Torr, a tip temperature of 25 K and a pulse to standing voltage ratio of 0.15.

III. Results

1. Electrochemical measurement

Figure 1 shows four cyclic polarization curves of the unaged and the aged cast duplex stainless steel in 0.5 kmol/m³ H₂SO₄+0.01 kmol/m³ KSCN solution. The peak at -100 mV and the shoulder at -300 mV in Fig. 1(a) corresponds to the active dissolution of the austenitic and ferritic phases, respectively. Ageing the steel for 400 h causes little change in the shape of the active current peak but increases the current in the passive region and the small reactivation current peak appears at -250 mV in the reverse sweep (shown as a broken line in Fig. 1(b)). The polarization curve in the reverse sweep is not shown in Fig. 1(a) because no positive current was recognized. After ageing for longer than 4000 h, the active current peak increases and the peak potential shifts to the positive direction (Fig. 1(c) and (d)). Furthermore, the reactivation current peak (represented by a broken line in the figures) grows. This current peak in the reverse sweep may be similar in nature to the reactivation peak obtained for the sensitized type 304 stainless steel. As discussed later, the reactivation current peak may be attributed to the presence of the chromium-depleted iron-

Fig. 1 Electrochemical potentiokinetic reactivation measurements as a function of ageing time (Solid lines represent the forward sweep and broken lines represent the reverse sweep).

Fig. 2 Composition change in the ferritic phase compared with in the austenitic phase as a function of ageing time. (Open symbols represent ferrite and solid symbols represent austenite.)

Fig. 3 SEM observation of the surfaces etched electrolytically in 10% oxalic acid. (a) unaged and aged for (b) 400 h (c) 4000 h and (d) 10000 h.

rich region which is formed as a result of phase decomposition of the ferritic phase during ageing.

2. Metallographic observations

Figure 2 shows the chemical compositional change of the ferritic and austenitic phase as a function of ageing

time determined by the energy dispersive X-ray analysis. No significant change appears in the chemical composition in the austenite. On the other hand in the ferritic phase silicon shows a gradual decrease with ageing and nickel and molybdenum show a considerable decrease by the prolonged ageing, while chromium remains constant

throughout the ageing. Figure 3 shows SEM micrographs of the etched surface as a function of ageing time. It should be noted that the unaged austenite is etched stronger than the ferritic phase, which is reasonable because of lower chromium concentration in the austenite than in the ferritic phase. On the other hand the aged ferritic phase is etched preferentially. This must be associated with the increase in the passive current and the change in the appearance of the reactivation peak with ageing. As described later, the ageing induces the phase decomposition in the ferritic phase, generating a large number of the chromium depleted iron-rich regions in the ferrite. As observed in the SEM photos the chromium depleted iron-rich region degrades the corrosion resistance of the ferrite phase, although individual size of it several nanometer thickness and width as determined by the POSAP, is too fine and too thin to be detected by the EDX. Furthermore minute pits are observed in the ferrite of the aged steel and their number and size increase with ageing. Since electrolytic etching with oxalic acid is known to etch precipitates such as carbides and nitrides, the presence of pits indicates the dissolution of some precipitates. Figure 4 shows the surface of the steel aged for 4000 h and 10000 h etched at 0 mV in 0.5 kmol/m³ H₂SO₄ + 0.01 kmol/m³ KSCN. Numerous precipitates are observed and the size and the density increase with ageing time. As observed in Fig. 4 precipitates remain un-

dissolved and chromium-depleted regions are preferentially dissolved by etching. A spot EDX analysis shows that the precipitates are rich in nickel, silicon, and molybdenum. The electron diffraction shows the precipitates being face centered cubic with a lattice constant of 1.06 nm⁽¹⁴⁾. These are likely to be G-phase observed in the aged type 308⁽¹⁵⁾ and CF8M⁽¹⁶⁾. Quantitative analysis is not possible because the precipitates are thin and fine. Precipitation of Ni-Si-Mo rich G-phase may lead to the decrease in nickel, silicon, molybdenum content in the ferritic phase for the longer aged steel as shown in Fig. 2.

3. Mechanical property change

Table 2 shows micro Vickers hardness of the ferritic phase and Charpy impact energy as a function of ageing time. The impact energy decreases with ageing while the hardness increases up to 4000 h ageing and then decreases with further ageing. It should be noted that the hardness of the austenitic phase shows little change during ageing. This indicates that the microstructural change in the ferritic phase is responsible for the hardening and the embrittlement.

4. POSAP analysis

Figure 5 shows typical Cr atom dot images of the sliced section obtained parallel to the specimen surface by a POSAP analysis. The image represents a slice approximately 1 nm in thickness and 20 nm in diameter. In the unaged steel (a), a uniform distribution of chromium atoms is seen, while in the aged steel (b), a separation of the chromium-rich and the chromium-depleted regions occurs.

Figure 6 shows the chromium concentration frequency distribution of the aged steel obtained with a sampling block size of 50 atoms without smoothing. In order to describe the frequency distribution corresponding to the degree of phase separation via spinodal decomposition, LBM model⁽¹⁷⁾ is usually used. The model allows the description of the frequency distribution corresponding to non-symmetrical concentration fluctuations. It assumes that the frequency distribution can be described as the sum of two Gaussians. In Fig. 6, the LBM simulation is also presented. A considerable deviation from the experimental distribution is seen, because in the experimental one, a multimodal distribution is observed, in which at least three peaks are observed. This sort of behaviour was noticed by Danoix *et al.*⁽⁶⁾ in the late stage of ageing at 400°C and by us⁽¹⁸⁾ at 450°C. This may indicate that

Fig. 4 SEM observation of the surfaces potentiostatically etched at 0 mV for 15 min after passivation at 200 mV. (a) aged for 4000 h (b) aged for 10000 h.

Table 2 Hardness in the ferritic phase and Charpy impact energy change as a function of ageing time at 450°C.

Ageing time, <i>t</i> /h	Hardness (<i>Hv</i> at 10 g)	Charpy impact energy/kgf-m
0	184	23.0
400	215	11.8
4000	258	6.2
10000	226	3.8

Fig. 5 Chromium atom dot images of the ferritic phase (An orthogonal slice of 1 nm in thickness and 20 nm in diameter).

Fig. 6 Chromium concentration frequency distribution for the steel aged for 10000 h. (a) Experimental distribution (b) LBM simulation.

the spinodal decomposition has already completed and the growth and aggregation of the precipitates occur. This coincides with the overageing behaviour indicated by the hardness measurement.

In order to visualize the microstructures developed in the aged steel, the isosurface 3-D reconstruction of the chromium-rich and the chromium-depleted regions is presented in Fig. 7. The surface of the chromium-rich regions are drawn through all points of Cr composition at 50 at%, while that of the chromium-depleted regions at 12 at%. Flat plate-like chromium-rich regions of a few nanometer thickness are observed at a spacing of a few nanometer, surrounded by the percolated Cr-depleted region. Loss of interconnectivity of the chromium-rich microstructures may suggest the completion of spinodal decomposition and the occurrence of growth and aggregation of the chromium-rich particles, which leads to a decrease in hardness.

IV. Discussion

In order to quantitatively determine the compositional development of the chromium-rich and the chromium-depleted regions, the chromium composition cross sections of 20 nm in diameter and 2 nm in thickness were generated from the POSAP data. The local composition of these images is represented by a grey scale from less than 12 at% Cr (black) for the chromium-depleted region to 50 at% or more (white) for the chromium-rich region. Figure 8 shows a typical example of the chromium composition cross section maps. Based on these composition cross section maps, the compositions in each grey scaled area are determined and the results are shown in Fig. 9. In addition to the chromium concentration variations, nickel concentration variation should be noted. Nickel concentration tends to increase in the chromium-depleted region and to decrease in the chromium-rich

Fig. 7 The isosurface 3-D reconstruction of the aged ferritic phase (A cylinder of 20 nm in diameter and 13 nm in height). (a) chromium-rich ($\text{Cr} \geq 50\text{ at\%}$) and (b) chromium-depleted ($\text{Cr} < 12\text{ at\%}$) regions.

Fig. 8 An example of the grey scale composition cross section map for chromium (Black: $\text{Cr} < 12\text{ at\%}$, white: $\text{Cr} \geq 50\text{ at\%}$, in between grey scaled as $\text{Cr} < 20\text{ at\%}$, $< 30\text{ at\%}$, $< 40\text{ at\%}$ and $< 50\text{ at\%}$).

Fig. 9 Composition of each grey scaled area appeared in the Cr composition cross section maps.

Fig. 10 The etched surface of the aged ferritic phase.

region. This agrees with the previous observation, in which nickel is excluded from the chromium-rich regions and absorbed in the chromium-depleted regions⁽⁶⁾. It should be noted that nickel concentration appears to be very low even in the chromium-depleted region as agreed with that determined by EDX (Table 2). The overall nickel concentration determined in the POSAP analysis (3.5 at%) is appears to be slightly lower than that of EDX.

The same can be applied to the molybdenum and silicon concentrations. Although molybdenum and silicon are known to preferentially partition to the chromium-rich region, little variation in concentration is observed among them. It appears that nickel, molybdenum and silicon are excluded either from the chromium-depleted or the chromium-rich regions and absorbed somewhere. This and the metallographic observations described above may suggest the precipitation of Ni-Si-Mo-rich G phase, though the POSAP analysis failed to detect. This phase is usually observed in the aged CF series duplex stainless steels⁽⁷⁾⁽⁸⁾. Figure 10 shows the enlarged view of the etched surface of the 10000 h aged steel. Small parti-

cles can be seen in the shallow pits where the dissolution takes place. The shallow pits must be dissolved chromium-depleted iron-rich regions and the particles may be identified as the G phase particles, which are known to precipitate at the interface of the chromium depleted and chromium-rich regions⁽⁷⁾⁽⁸⁾. During the dissolution of chromium-depleted iron-rich regions, fine chromium-rich regions surrounded by chromium-depleted iron-rich regions in a form of percolated structure are removed. This promotes the penetration and may create the pits shown in the SEM photos, while coarse G phase particles remain in the pits. Because of the G phase precipitation, nickel, silicon and molybdenum concentration decrease in the chromium-depleted region as well as in the chromium-rich region. The composition in the chromium-depleted region of the Cr concentration less than 12 at% in the 25Cr-6Ni-3Mo duplex stainless steel aged at 450°C for 5000 h which does not show any evidence of G phase precipitation is 11.8Cr-8.0Ni-2.7Si-1.2Mo. This clearly indicates that without G phase precipitation nickel tends to segregate in the chromium-depleted region. Failure of the detection of G phase by the POSAP can be simply accounted for by its low volume fraction. Nickel, silicon and molybdenum are excluded from the chromium-depleted and the chromium-rich regions and absorbed in the G phase.

The composition in the chromium depleted region of the Cr concentration less than 12 at% in the present steel is 10.9Cr-4.1Ni-0.6Si-0.5Mo and it surrounds the chromium rich region as viewed in Fig. 7. Although the chromium depleted region is fine and thin, owing to its lowered Cr concentration and considerable fraction, it readily induces the loss of the passivity and the reactivation during the reverse sweep in the cyclic polarization. This is reflected in the increase in the current density in the passive region by an order of magnitude and in the preferential etching of the ferritic phase by the electrolytic etching in oxalic acid. The reactivated dissolution of this region results in the shallow pit as shown in Fig. 10. It can be concluded that the decrease in the Cr concentration to less than 12 at% in this region must be responsible for the reactivation, similar to the sensitized austenitic stainless steels in which the reactivation has been attributed to the chromium depleted zone of less than 12 at%Cr in the vicinity of the grain boundary⁽¹⁹⁾.

V. Summary

Electrochemical potentiokinetic reactivation measure-

ments and metallographic observation were performed on the cast duplex stainless steel of CF3M aged at 450°C for up to 10000 h. In addition a detailed POSAP analysis was made for the steel aged for 10000 h. The reactivation current peak appears after 400 h ageing, where the preferential dissolution of the ferritic phase begins to occur in the electrolytic oxalic acid etching. This is attributed to the formation of the chromium-depleted iron-rich region due to the phase decomposition of the ferritic phase.

The POSAP analysis shows well developed phase decomposition into flat plate-like chromium-rich region of a few nanometer thickness and the chromium-depleted iron-rich region of the percolated structure.

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