

Effect of Ethanolamines on Corrosion Inhibition of Ductile Cast Iron in Nitrite Containing Solutions

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In this work, synergistic corrosion inhibition effect of nitrite and 3 kinds of ethanolamines on ductile cast iron using chemical and electrochemical methods was evaluated. This work attempts to clarify the synergistic effect of nitrite and ethanolamines. The effects of single addition of TEA, DEA, and MEA, and mixed addition of nitrite plus TEA, DEA or MEA on the corrosion inhibition of ductile cast iron in a tap water were evaluated. A huge amount of single addition of ethanolamine was needed. However, the synergistic effect by mixed addition was observed regardless of the combination of nitrite and triethanolamines, but their effects increased in a series of MEA + nitrite > DEA + nitrite > TEA + nitrite. This tendency of synergistic effect was attributed to the film properties and polar effect; TEA addition couldn't form the film showing high film resistance and semiconductive properties, but DEA or MEA could build the film having relatively high film resistance and n-type semiconductive properties. Moreover, it can be explained that this behaviour was closely related to electron attractive group within the ethanolamines, and thus corrosion inhibition power depends upon the number of the electron attractive group of MEA, DEA, and TEA.

Keywords : corrosion inhibitor, ductile cast iron, nitrite, ethanolamine, synergistic effect

1. Introduction

Corrosion inhibitors can be divided into anodic passivating, cathodic precipitation, and adsorption organic inhibitors¹⁾; Anodic inhibitors increase anodic polarization to the critical protection potential of the metal or alloys. They are called passivating inhibitors because they drastically decrease the corrosion current. Cathodic precipitation inhibitors decrease the corrosion rate by increasing the cathodic polarization overvoltage (hydrogen and oxygen reduction). Thick deposits form in the presence of these inhibitors and decrease depolarizer diffusion to the metal surface, inhibiting the cathodic reaction and corrosion. Organic corrosion inhibitors contain sulfur, nitrogen, or oxygen atoms and organic heterocyclic compounds containing polar groups²⁻⁶⁾. These compounds adsorb and form a covalent bond on the metal surface⁷⁾. Organic inhibitors cover the entire surface area of the corrosion metal with a thick film consisting of several monolayers and change the structure of the double layer at the

metal interface, decreasing depolarization rate. They may also act as a barrier film by blocking anodic and cathodic active sites or decreasing electroactive species transport rate to or from the metal surface⁷⁾.

There are many reports on the corrosion inhibition by nitrite, including Fe₂O₃ formation on steel by nitrite addition⁸⁾, adherent protective oxide on steel⁹⁾, correlation of oxygen and nitrite on steel¹⁰⁾, and comparative study of nitrite including various inhibitors on steel¹¹⁻¹³⁾. Nitrite has a tendency to increase anodic polarization and thus increase corrosion potential to a noble direction and reduce the corrosion rate. Since nitrite has a strong oxidizing power, it makes the surface film on steel and thus shows good performance¹⁴⁾. In the case of ductile cast iron, however, a huge amount of nitrite was needed to form a stable protective film. In recent, K. T. Kim and co-workers reported the corrosion inhibiting mechanism of nitrite ion on the passivation of carbon steel and ductile cast iron¹⁵⁾; While NaNO₂ addition can greatly inhibit the corrosion of carbon steel and ductile cast iron, *ca.* 100 times more NaNO₂ addition is needed for ductile cast iron than for carbon steel in order to improve the similar corrosion resistance.

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Table 1. Chemical composition of the experimental alloy

Material	Chemical composition, wt%									
	C	Mn	P	S	Si	Cu	Mo	Ni	V	Fe
Ductile Cast Iron (DCI)*	4.008	0.173	0.022	0.026	1.528	0.023	0.028	0.059	0.016	bal.

*KS D4311

A corrosion and inhibition mechanism was proposed whereby nitrite ion is added to oxidize. The nitrite ion can be reduced to nitrogen compound and this compound may be absorbed on the surface of graphite. Therefore, since nitrite ion needs to oxidize the surface of matrix and needs to passivate the galvanic corroded area and since it is absorbed on the surface of graphite, a greater amount of corrosion inhibitor needs to be added to ductile cast iron than to carbon steel.

Ethanolamine is one of representative organic corrosion inhibitors and is also adsorption type. There are 3 kinds of ethanolamines – monoethanolamine (MEA), diethanolamine (DEA), and triethanolamine (TEA). All of them have a good corrosion inhibition effect¹⁶⁾. Also, when anodic passivating inhibitor and adsorption type inhibitor were co-existed, synergistic effect of them was reported¹⁷⁻²⁰⁾. Recently, when nitrite ion was added with triethanolamine, we evaluated the synergistic effect and proposed its mechanism²¹⁾, but there is no report on the inhibition mechanism about mixed additions with diethanolamine or monoethanolamine.

In this work, therefore, synergistic corrosion inhibition effect of nitrite and 3 kinds of ethanolamines on ductile cast iron using chemical and electrochemical methods was evaluated. This work attempts to clarify the synergistic effect of nitrite and ethanolamines.

2. Experimental procedure

2.1 Materials and corrosion environments

Ductile cast iron (KS D4311)²²⁾ was used in this work. Table 1 shows the chemical composition of the experimental alloy. The test solution was a tap water with or without inhibitors. Nitrite (as NaNO₂) and ethanolamines added in concentrations of the order of ppm.

2.2 Corrosion tests

Immersion corrosion test: A specimen was cut to a size of 20 × 20 × 5 mm and each surface of this specimen was ground using #120 SiC paper. Immersion tests were conducted in 500 mL glass flask containing stagnant

solution. Test time was 72 hrs. After performing the immersion test, each specimen was cleaned with acetone and alcohol. Then, this specimen was dried. Finally, the corrosion rate of this specimen was determined.

Electrochemical tests: Specimens were cut to a size of 20 × 20 mm. After connecting these specimens in an electrical circuit, they were epoxy-mounted. Then, the surface of these specimens was ground using #600 SiC paper. Finally, these specimens were coated with epoxy resin, except an area of 1 cm². A polarization test was performed using a potentiostat (DC105, Gamry Instruments), the reference electrode was a saturated calomel electrode, and the counter electrode was Pt wire. The test solution was deaerated using nitrogen gas: this gas was purged at a rate of 200 mL/min into the solution for 30 minutes. The scanning rate was 0.33 mV/sec. In order to measure the AC impedance, the specimens were ground using #2,000 SiC paper. Then, these specimens were polished using a diamond paste (its diameter was 3 μm). The test solution was same as that used in polarization test. To measure AC impedance, we used an electrochemical analyzer (EIS 300, Gamry Instruments). Before measuring AC impedance, passivation was performed on ductile cast iron at +0.2 V and 0 V(SCE) for 30 minutes. AC impedance was measured ranging from 10 kHz to 0.01 Hz and the AC voltage amplitude was 10 mV. Thereafter, a Mott-Schottky plot was constructed to determine the semi-conductive properties of the passive film. The specimen preparation was the same as that used in the measurement of AC impedance, and the DC amplitude was 10 mV (peak-to-peak) at 1,580 Hz of AC frequency²³⁾. The capacitance was measured at a scan rate of 50 mV/sec: the potential was varied between +1.5 V(SCE) to -1.5 V(SCE).

Surface analysis; X-ray Photoelectron spectroscopy (XPS, K-alpha (Thermo VG, U.K.), Al-K_α (1486.6 eV, 12 kV, 3 mA)) was performed to determine the chemical state of several species in the passive film. The specimen was cut to a size of 20 × 20 × 5 mm, and it was ground with #2000 SiC paper. Thereafter, it was polished with a diamond paste, which was 3 μm in diameter. Finally,

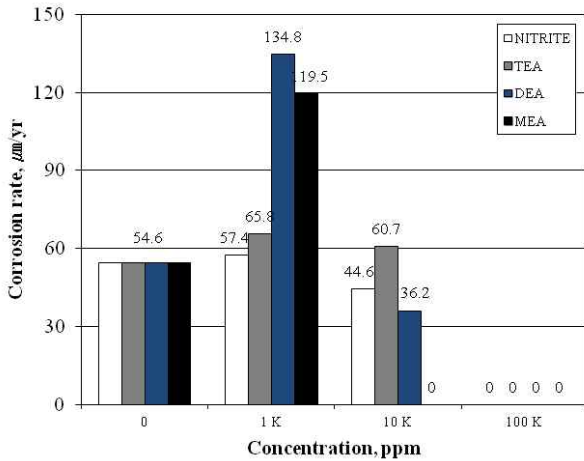


Fig. 1. The effect of single addition of corrosion inhibitor on the corrosion rates of DCI (25 °C tap water + x ppm corrosion inhibitor).

the specimen was cleaned with alcohol using an ultrasonic cleaner. Ductile cast iron was passivated by immersing it in 100,000 ppm TEA, DEA, MEA, 1,000 ppm nitrite

+ 2,500 ppm TEA, 1,000 ppm nitrite + 1,500 ppm DEA, 1,000 ppm nitrite + 1,000 ppm MEA respectively. The immersion process was carried out for 72 hours. The depth profile was obtained every 5 seconds by Ar-sputtering. In addition, an Electron Probe Micro Analyzer (EPMA, EPMA-1600, 15KV) was used to identify the elemental distribution of passivated surface. Optical Microscope (OM, Zeiss Axiotech 100HD) and scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM (Tescan Vega II LMU) EDS (OXFORD ISIS-300)) were used. Furthermore, to investigate the surface compounds.

3. Results and Discussion

In this work, two kinds of corrosion inhibitors were used; anodic passivating and organic adsorption types. An anodic passivating inhibitor can inhibit the metal by the formation of passive film and precipitation, which they block the metal surface to corrosion environments. One of the representative inhibitors is nitrite. Recently, we re-

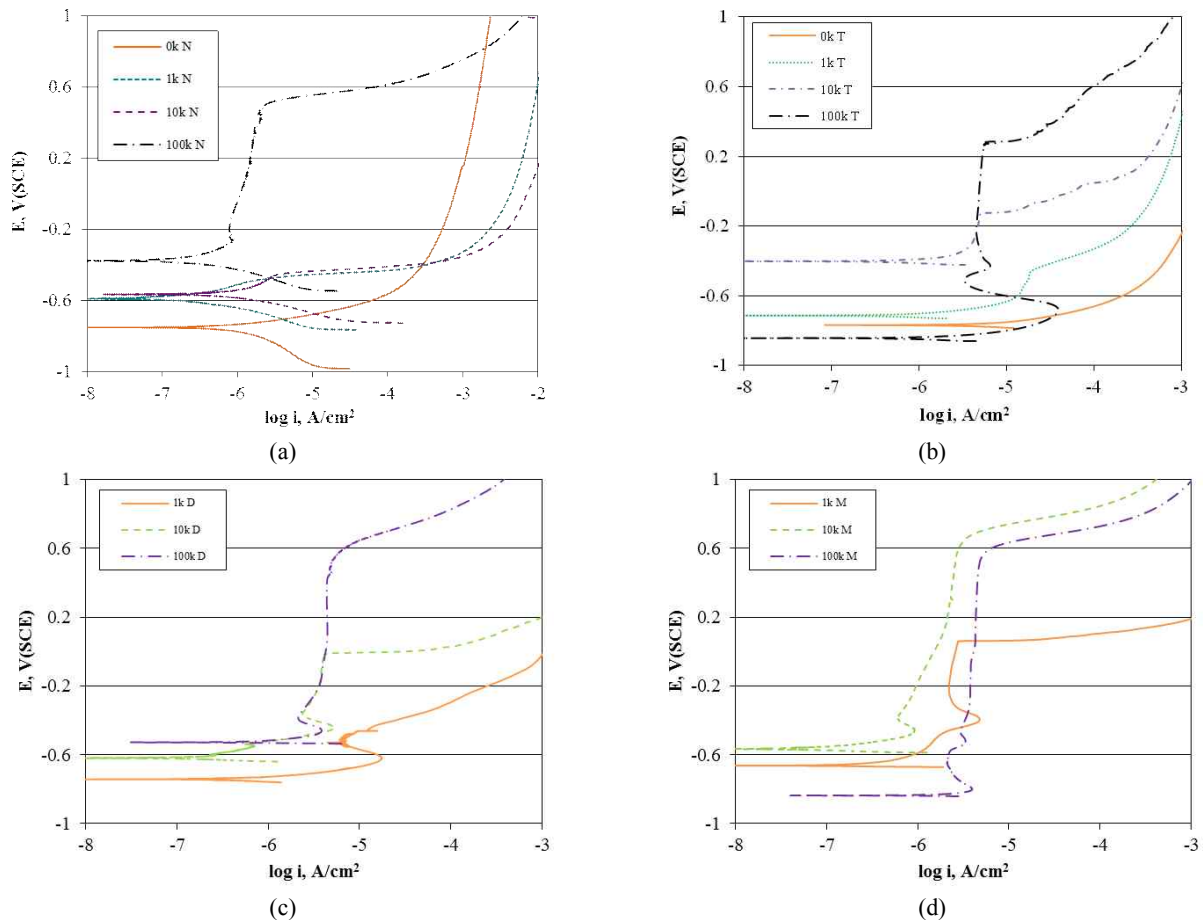


Fig. 2. Effect of single added corrosion inhibitors on anodic polarization curve of DCI (25 °C deaerated tap water + x ppm corrosion inhibitor); (a) N (NITRITE), (b) T (TEA), (c) D (DEA), (d) M (MEA).

ported the mechanism about nitrite addition on corrosion inhibition of carbon steel and ductile cast iron¹⁵; the passive film of carbon steel and ductile cast iron, formed

by NaNO_2 addition showed N-type semi-conductive properties and its resistance was increased; the passive current density was thus decreased and the corrosion rate was then lowered. In addition, the film was mainly composed of iron oxide due to the oxidation by nitrite ion; however, regardless of the alloys, nitrogen compounds (not nitrite) were detected at the outermost surface, but were not incorporated in the inner oxide. Fig. 1 shows the effect of single addition of corrosion inhibitor on the corrosion rates of ductile cast iron. When any inhibitors were not added to a tap water, the corrosion rate of ductile cast iron was determined as $54.6 \mu\text{m/y}$. Regardless of corrosion inhibitors, 1 k ppm addition of inhibitors reversely increased the corrosion rate of the iron. Finally, 100 k ppm addition of inhibitors completely inhibited the corrosion of ductile cast iron in a tap water. This behavior can be arisen because insufficient addition of inhibitors couldn't overcome the galvanic corrosion between the matrix and graphite of ductile cast iron¹⁵. As shown in Fig. 1, complete corrosion inhibition of ductile cast iron in a tap water needs a huge concentration as 100 k ppm, regardless of corrosion inhibitors, and this concentration is not practical in engineering fields.

Fig. 2 represents the effect of single added corrosion inhibitors on the anodic polarization curves of ductile cast iron. Nitrite, anodic passivating inhibitor, couldn't build the stable passive film till 10 k ppm, but 100 k ppm nitrite addition, finally, formed the stable passive film. In the case of triethanolamine, 100 k ppm addition formed the stable passive film but the transpassive potential relatively was low. 100 k ppm addition of diethanolamine built the stable passive film. Also, in the case of monoethanolamine, 10 k and 100 k ppm additions show the stable passivation behavior. It should be noted that all inhibitors need a large concentration to inhibit the corrosion of ductile cast iron in a tap water, as like chemical immersion corrosion tests in Fig. 1.

Fig. 3 shows the effect of co-added corrosion inhibitors on the anodic polarization curves of ductile cast iron in a tap water. In the case of mixed addition of nitrite and triethanolamine, even 1k ppm nitrite plus 2.5 k ppm TEA could build the stable passive film. In the case of nitrite and diethanolamine, 1 k ppm nitrite plus 1.5 k ppm DEA showed the stable passive range. Especially, in the case of nitrite and monoethanolamine, 1 k ppm nitrite plus 1 k ppm MEA built the stable passive film. In summary, mixed addition of nitrite and ethanolamines greatly reduced the inhibitor concentration to inhibit the corrosion of ductile cast iron in a tap water, regardless of the types of ethanolamine. Also, its inhibition effect was highly evaluated as a series of $\text{MEA} > \text{DEA} > \text{TEA}$. If it is

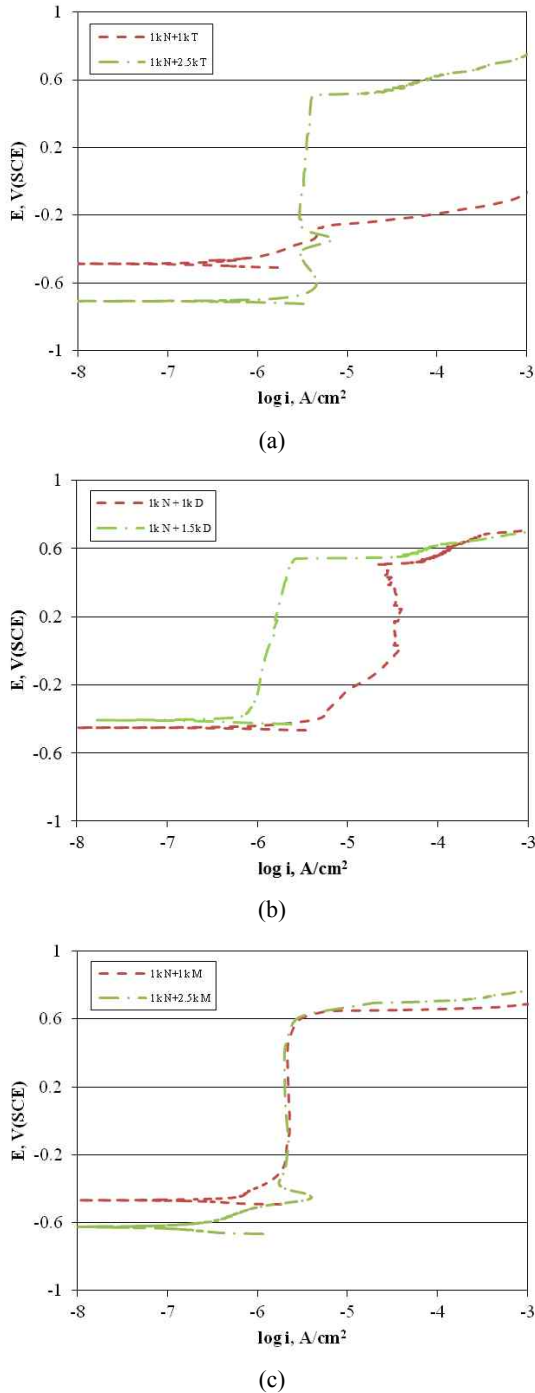


Fig. 3. Effect of mixed added corrosion inhibitors on anodic polarization curve of DCI (deaerated tap water + x ppm ethanolamines + 1k ppm NITRITE); (a) NITRITE + TEA, (b) NITRITE + DEA, (c) NITRITE + MEA.

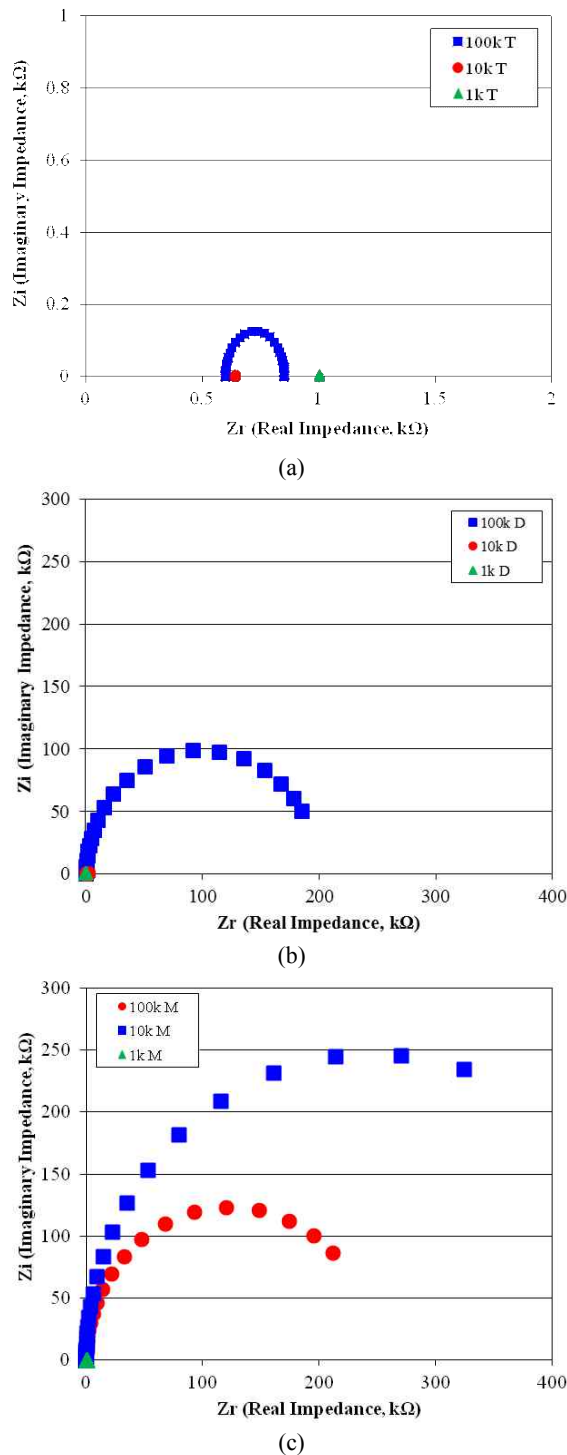


Fig. 4. Effect of corrosion inhibitors on AC impedance of the passive film formed at 0 V(SCE) in deaerated tap water at 30 °C; (a) T (TEA), (b) D (DEA), (c) M (MEA).

so, do they inhibit the corrosion of ductile cast iron with the same inhibition mechanism?

Fig. 4 shows the effect of corrosion inhibitors on AC

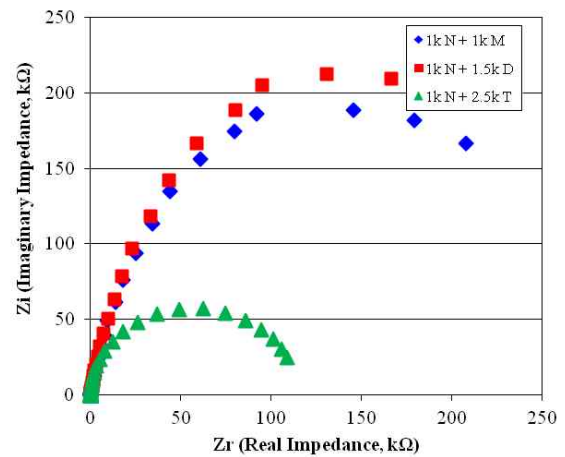
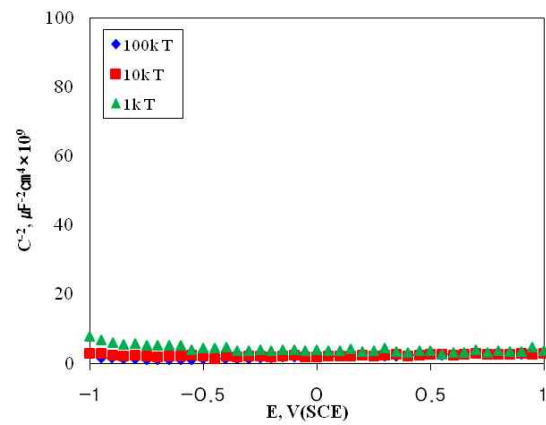


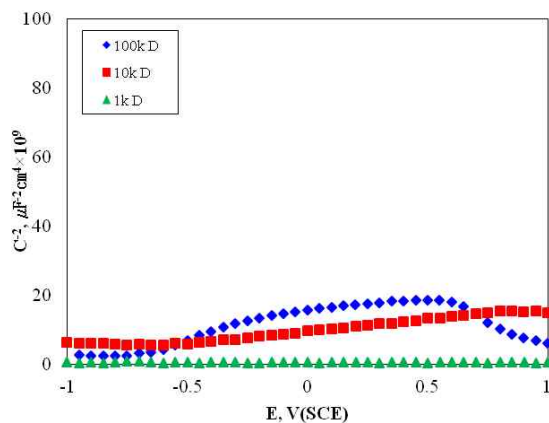
Fig. 5. Effect of mixed corrosion inhibitors on AC impedance of the passive film formed at 0 V(SCE) in deaerated tap water at 25 °C; (N : NITRITE, T: TEA, D: DEA, M: MEA).

impedance of the passive film formed at 0 V(SCE) in deaerated tap water. When the concentration of single TEA addition increased, AC impedances were very low values. However, 100 k ppm DEA addition greatly increased the AC impedance, and 10 k ppm and 100 k ppm MEA, also, drastically increased the impedances. This means that the film resistance was increased because of high concentration inhibitors, and these films blocked the ductile cast iron from the corrosion environment. This tendency was increased in a series of MEA > DEA > TEA. Fig. 5 shows the effect of mixed corrosion inhibitors on AC impedance of the passive film formed at 0 V(SCE) in deaerated tap water. Mixed concentration was optimum value as determined in Fig. 3. AC impedance of nitrite plus TEA was relatively low and the impedances of both nitrite plus DEA and nitrite plus MEA were high values and also similar to each other.

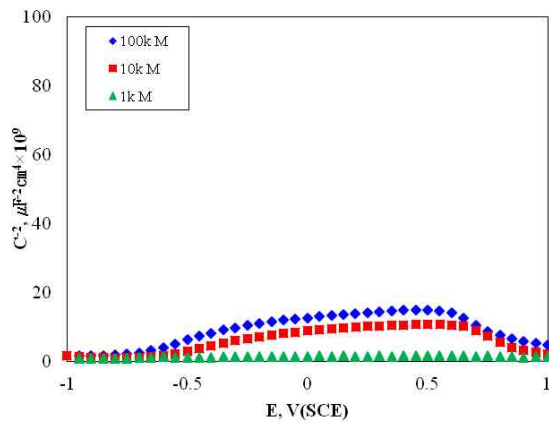
Fig. 6 shows the effect of single corrosion inhibitors on Mott-Schottky plot for the passive film formed at 0 V(SCE) in deaerated tap water. In the case of single nitrite addition¹⁵⁾, the surface film showing n-type semiconductive properties was formed by increasing nitrite concentration. However, single TEA addition didn't form the semiconductive film, but in the case of single DEA and single TEA additions, the films of low level n-type semiconductive properties were built on the surface only at a high concentration. In the case of mixed additions as shown in Fig. 7, the films formed at optimum concentration revealed the low level n-type semiconductive properties. In other words, TEA addition couldn't form the film showing high film resistance and semiconductive properties, but DEA or MEA addition could build the film having relatively high film resistance and n-type semi-



(a)



(b)



(c)

Fig. 6. Effect of single corrosion inhibitors on Mott-Schottky plot for the passive film formed at 0 V(SCE) in deaerated tap water at 30 °C; (a) TEA, (b) DEA, (c) MEA.

conductive properties.

Fig. 8 shows the elemental distribution analyzed by EPMA on the surface of ductile cast iron, which was passivated for 72 hours in tap water with 100 k ppm corrosion

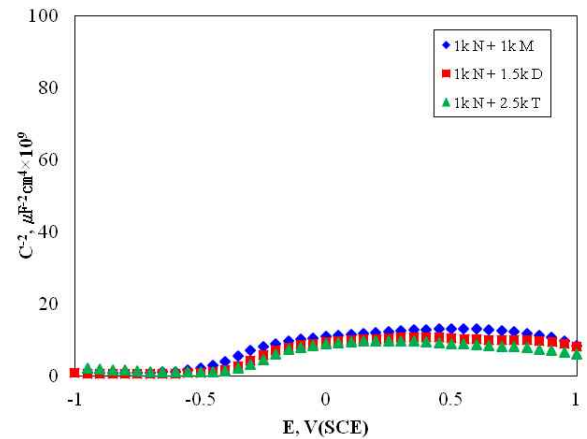


Fig. 7. Effect of corrosion inhibitors on Mott-Schottky plot for the passive film formed at 0 V(SCE) in deaerated tap water at 25 °C; (N : NITRITE, T: TEA, D: DEA, M: MEA).

inhibitors. (a, b, c) means oxygen distribution and (a', b' c') implies nitrogen distribution. Oxygen and nitrogen amounts on the surface increase qualitatively in a series of MEA > DEA > TEA, and also both elements were accumulated near the graphite. These adsorbed layers could prevent the galvanic corrosion between the matrix and graphite. In the case of mixed corrosion inhibitors, oxygen and nitrogen were also accumulated near the graphite as like the single addition.

Fig. 10 shows the XPS depth profile and N_{1s} peaks of the surface film formed in 100 k ppm corrosion inhibitors. In the case of TEA and MEA, oxygen accumulated at the outer surface till about sputtering time of 60 seconds, but in the case of DEA, thick oxide layer was observed still after sputtering time of 150 seconds. Even though nitrogen element was detected on the surface by EPMA, however, nitrogen peak was detected only at the outmost surface. This means that oxygen presents in a relatively thick layer but nitrogen presents in the outmost film even in high concentration of ethanolamines. Fig. 11 shows the XPS profile and N_{1s} peaks of the surface film formed in the optimum concentration of each mixed inhibitors as determined in Fig. 3. Regardless of the combination of inhibitors, oxygen was detected in an outer surface layer and nitrogen presents only at the outmost surface.

In order to inhibit the corrosion of ductile cast iron in a tap water, 100 k ppm triethanolamine was needed and we proposed the inhibition mechanism earlier¹⁵; A corrosion and inhibition mechanism was proposed whereby nitrite ion is added to oxidize. The nitrite ion can be reduced to nitrogen compound and this compound may absorb on the surface of graphite. Therefore, since nitrite ion needs

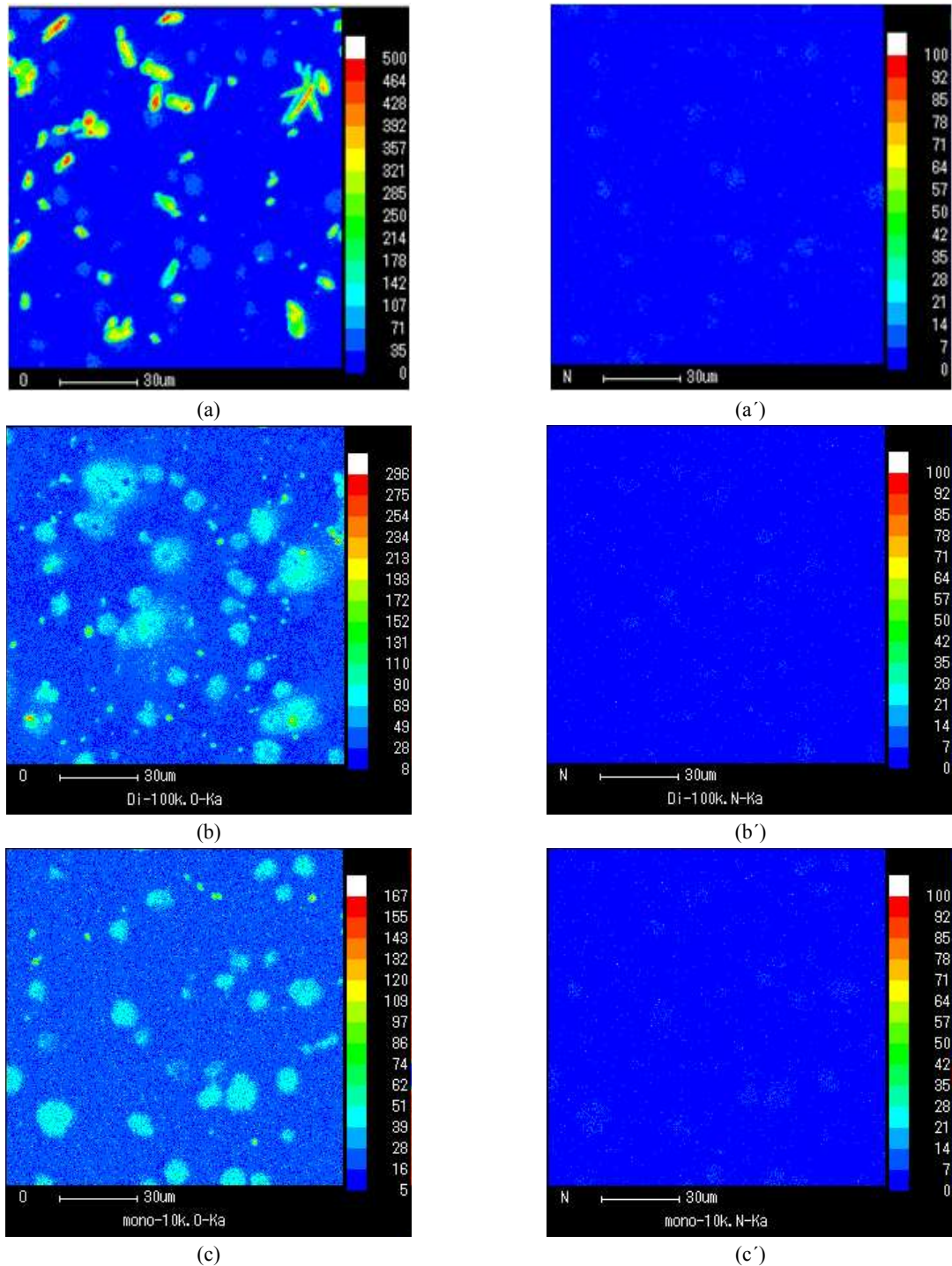


Fig. 8. Elemental distribution analyzed by EPMA on the surface of DCI, (a, b, c) oxygen and (a' b' c') nitrogen, which was passivated for 72 hours in tap water with 100 k ppm corrosion inhibitors at 25 °C; (a, a') TEA, (b, b') DEA, (c, c') MEA.

oxidize the surface of matrix and needs to passivate the galvanic corroded area, and since it is absorbed on the surface of graphite, a greater amount of corrosion inhibitor needs to be added to ductile cast iron than to carbon steel. Also, mixed addition of nitrite and triethanolamine greatly

reduced the concentration of mixed inhibitors to 1/30 times and also we proposed the mechanism on synergistic effect, recently²¹⁾; Owing to the synergistic effect of nitrite and TEA, there was effective inhibition of corrosion of DCI in tap water: the inhibitory effect was *ca.* 30 times

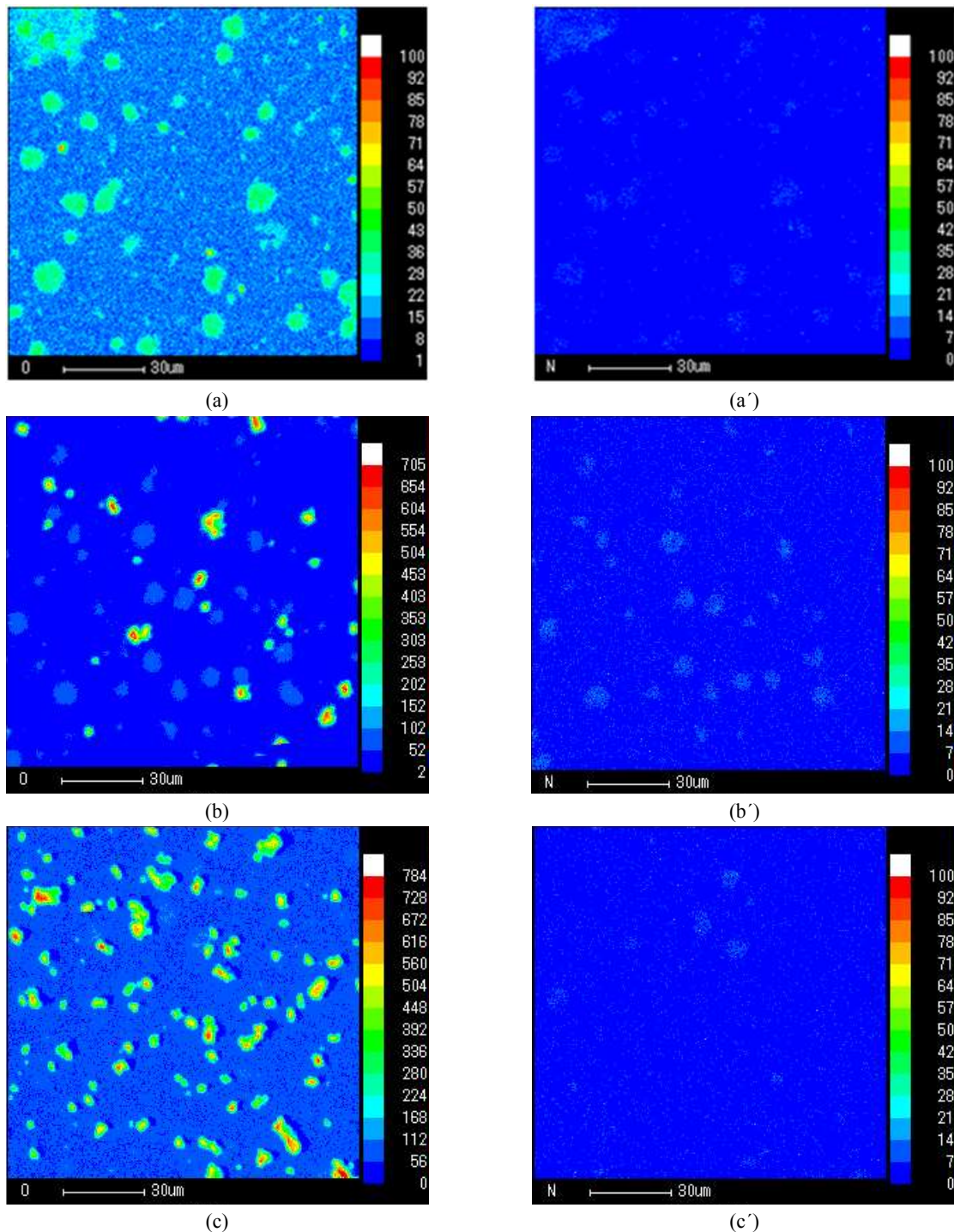


Fig. 9. Elemental distribution analyzed by EPMA on the surface of DCI, (a, b, c) oxygen and (a' b' c') nitrogen, which was passivated for 72 hours in tap water with x ppm corrosion inhibitors at 25 °C; (a, a') N + T, (b, b') N + D, (c, c') N + M.

more effective than that witnessed with single additions. This synergistic effect occurs by the following process; among the two inhibitors, nitrite oxidizes the metallic surface. On the other hand, TEA gets adsorbed simultaneously at the graphite surface. This adsorbed layer acts

as the barrier layer that mitigates the galvanic corrosion between graphite and matrix. Finally, synergistic effect is achieved.

In this paper, we performed the comparative studies about the effects of single addition of TEA, DEA, and

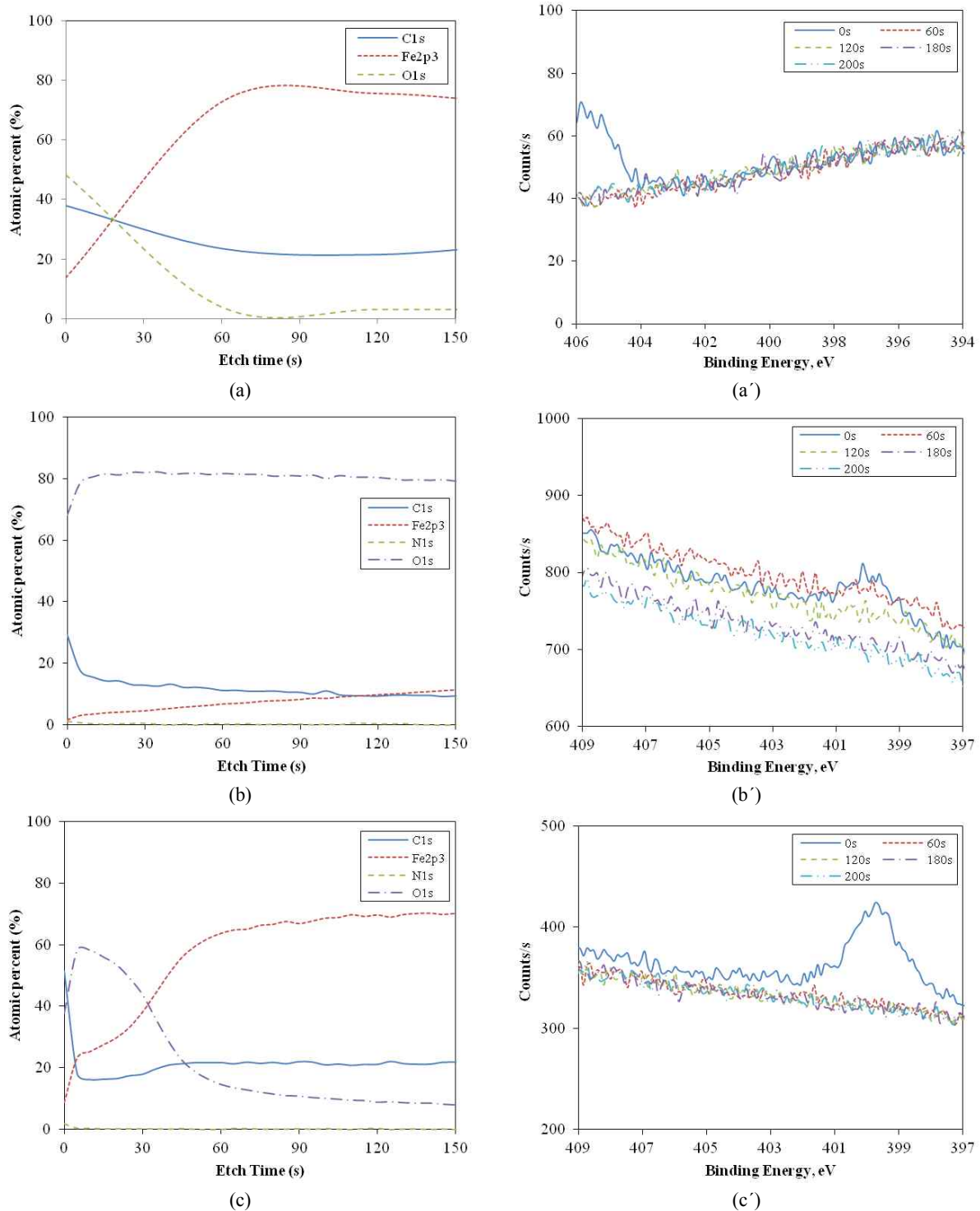


Fig. 10. XPS depth profile (a, b, c) and Ni_{2p} peaks (a', b', c') of the surface film formed in (a, a') 100k ppm TEA, (b, b') 100k ppm DEA, (c, c') 100k ppm MEA.

MEA, and also, of mixed addition of nitrite plus DEA or MEA. The synergistic effect was observed regardless of the combination of nitrite and triethanolamines, but their effects increased in a series of MEA + nitrite > DEA +

nitrite > TEA + nitrite. This difference of synergistic effect was attributed to the film properties and polar effect²⁴; TEA addition couldn't form the film showing high film resistance and semiconductive properties, but DEA or

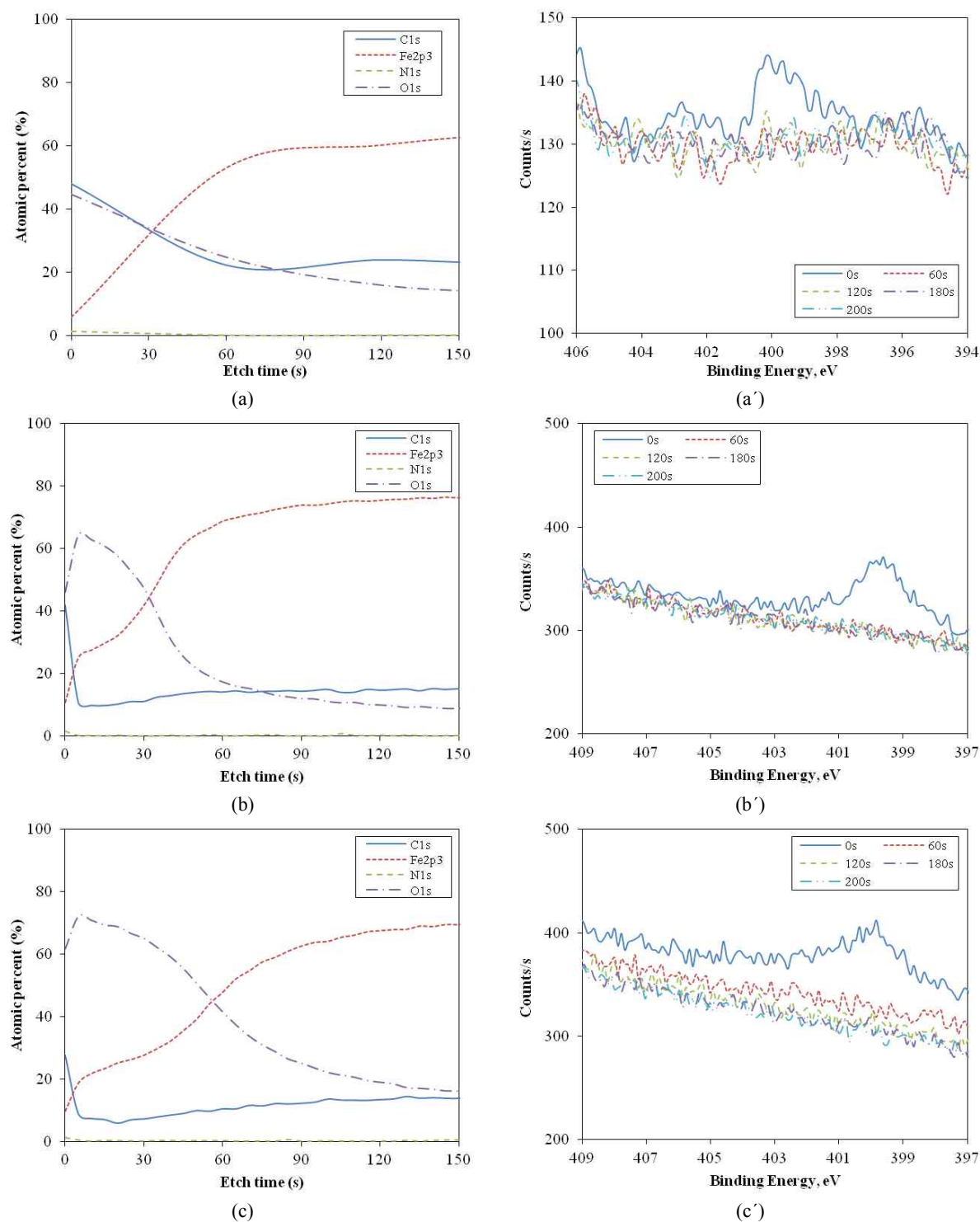


Fig. 11. XPS depth profile (a, b, c) and N_{1s} peaks (a', b', c') of the surface film formed in (a, a') 1k ppm NITRITE + 2.5k ppm TEA, (b, b') 1k ppm NITRITE + 1.5k ppm DEA, (c, c') 1k ppm NITRITE + 1k ppm MEA.

MEA could build the film having relatively high film resistance and n-type semiconductive properties. Moreover, it can be explained that this behaviour was closely related

to electron attractive group within the ethanolamines^{25,26}. Electron attractive group is the functional group showing negative inductive effect. This negative inductive effect pulled

the unshared electron pair of nitrogen atom - active centre and then reduced the electron density - adsorption centre. Therefore, they finally reduced the adsorption power of the corrosion inhibitor and thus corrosion inhibition power depends upon the number of the electron attractive group of MEA, DEA, and TEA.

5. Conclusions

1) The effects of single addition of TEA, DEA, and MEA, and mixed addition of nitrite plus TEA, DEA or MEA on the corrosion inhibition of ductile cast iron in a tap water were evaluated. A huge amount of single addition of ethanolamine was needed. However, the synergistic effect by mixed addition was observed regardless of the combination of nitrite and triethanolamines, but their effects increased in a series of MEA + nitrite > DEA + nitrite > TEA + nitrite.

2) This tendency of synergistic effect was attributed to the film properties and polar effect; TEA addition couldn't form the film showing high film resistance and semiconductive properties, but DEA or MEA could build the film having relatively high film resistance and n-type semiconductive properties. Moreover, it can be explained that this behaviour was closely related to electron attractive group within the ethanolamines, and thus corrosion inhibition power depends upon the number of the electron attractive group of MEA, DEA, and TEA.

Acknowledgments

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