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Electrochemical Analysis of the Microbiologically Influenced Corrosion of Steels by Sulfate-Reducing Bacteria

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We have investigated the differences between the general corrosion and microbiologically influenced corrosion (MIC) of steels in terms of electrochemical behavior and surface phenomena.

Corrosion potential of steels in the absence of SRB (sulfate-reducing bacteria) shifted to a low level and was maintained throughout the experimental period (40 days). The potential in the presence of SRB, however, shifted to a noble level after 20 days' incubation, indicating the growth of SRB biofilms on the test metal specimens and a formation of corrosion products. In addition, the color of medium inoculated with SRB changed from gray to black. The color change appeared to be caused by the formation of pyrites (FeS) as a corrosion product while no significant color change was observed in the medium without SRB inoculation.

Moreover, corrosion rates of various steels tested for MIC were higher than those in the absence of SRB. This is probably because SRB were associated with the increasing corrosion rates through increasing cathodic reactions which caused reduction of sulfate to sulfide as well as formation of an oxygen concentration cell. The pitting corrosions were also observed in the SRB-inoculated medium.

Keywords : *microbiologically influenced corrosion, corrosion potential, sulfate-reducing bacteria, biofilm, pitting corrosion*

1. Introduction

Although microbiologically influenced corrosion researches were started about 100 years ago, most microbial corrosion studies were carried out in1980's because the significance of corrosion damages was known recently. For the first time Gaines,[1] however, suggested that corrosion at the inner and outer sides of a water pipe was influenced with sulfide-oxidizing bacteria and iron-oxidizing bacteria.

Recently with a rapid development of industries many structural steels were exposed to severe corrosive environments, so that development of corrosion resistant steels was necessary in terms of both economical and industrial safety viewpoints. Unexpected accidents caused by a structural corrosion often happened. For examples, water pipe line leaked due to the corrosion of welded area of stainless steel pipe inspected safe,[2)-4)] and unexpected severe pitting corrosions in cargo oil tank bottom plating were also observed.[5)] Corrosion damages of fuel oil tank in aircraft as well as the abnormal corrosion of weld metal area of stainless steels were reported.[6)-7)]

A series of corrosion accidents mentioned above were not significant compared with conventional corrosion based on the electrochemical theory is a simple concept. Eventually it was, however, thought that the origin of corrosion was attributed to microorganism existing in various corrosive environments. Furthermore it was reported that the corrosion damage associated with bacteria in some places such as a petroleum chemical industry, a nuclear power generating plant and concrete structures frequently happened and the amounts of damage were estimated to be over several billion dollars.[8)-9)]

In this study, the susceptibility of TMCP (Thermo Mechanical Control Process) steel, Normalized steel and conventional Mild steel to MIC caused by SRB was investigated based on the electrochemical aspects. The objectives of this study were to compare MIC susceptibilities of some steels of industrial use and to examine the differences of polarization behaviors resulting from the MIC among the steels.

2. Experimental

2.1 Corrosion cell and test specimens

After the surface of test specimen was polished with the sand paper (No. 1000) and degreased with acetone, it was insulated with an epoxy coating leaving 1cm^2 area uncoated for the corrosion test. A microcosm (500 ㎖ beaker) was used as a corrosion test cell. The sterilized liquid medium (300 ㎖) was prepared in the cell and 30 ㎖ of SRB of stationary phase was inoculated. A rubber stopper of the beaker carried inlet & outlet holes for injecting nitrogen gas and hole for inserting a salt bridge of reference electrode and was surface-sterilized with 70% ethanol before the experiment. The experimental apparatus was shown in Fig. 1 and Table 1 showed chemical composition of the test specimens.

2.2 SRB and liquid medium

SRB used in this study were obtained from Korean Collection of Type Cultures (Korea Research Institute of Bioscience and Biotechnology, Taejon, Korea) and were isolated from a crude oil sample. The purchased strain was *Desulfovibrio gigas* (KCTC 2483) *Desulfovibrio vulgaris* (KCTC 1910) and the environmental isolates were KMU-1 (large colony type) and KMU-2 (small colony type) and were preserved permanently in liquid medium

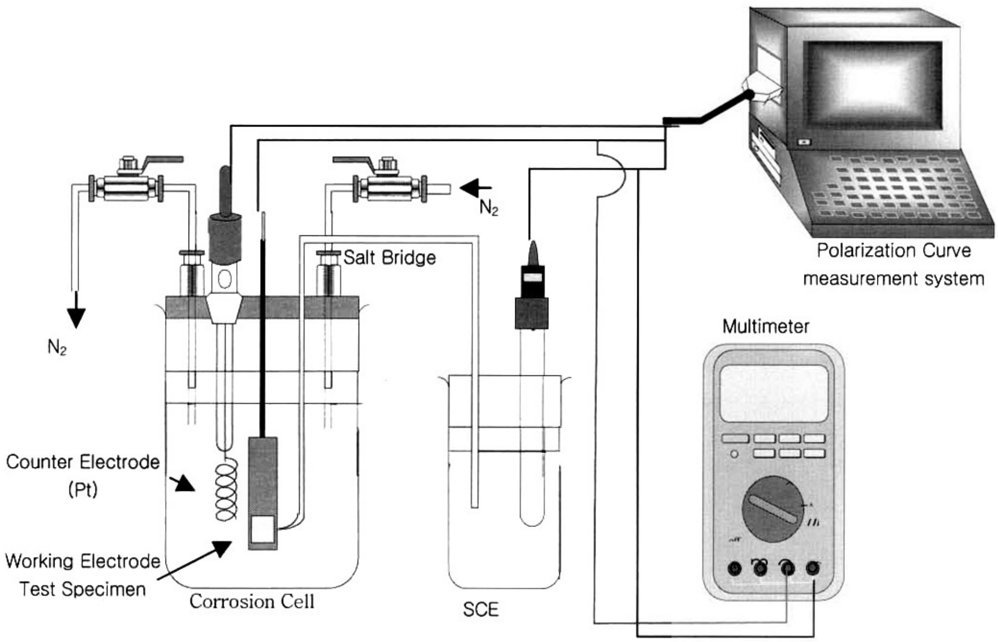

Fig. 1. Schematic diagram of the experimental apparatus for corrosion test

Table 1. Chemical composition of steel specimens used for the corrosion test.[1]

[1] % (w/w)

Sample	C	Si	Mn	P	S	Cu	Ni	V	Nb	Remark
Mild steel, A grade	0.144	0.162	0.663	0.014	0.005	0.007	0.024	0.005	-	σ_y : 24 kgf/㎟
Mild steel, E grade	0.105	0.178	1.12	0.019	0.005	0.007	0.015	0.003	-	σ_y : 24 kgf/㎟
Normalized steel, AH36	0.110	0.288	1.34	0.011	0.005	0.007	0.011	0.005	-	σ_y : 36 kgf/㎟ σ_{max} : 50~63 kgf/㎟
Normalized steel, AH32	0.136	0.158	1.05	0.013	0.007	0.006	0.010	0.005	-	σ_y : 32 kgf/㎟ σ_{max} : 48~60 kgf/㎟
TMCP steel, EH36	0.148	0.457	1.46	0.017	0.005	0.009	0.020	0.037	0.028	σ_y : 36 kgf/㎟ σ_{max} : 50~63 kgf/㎟
TMCP steel, DH36	0.173	0.435	1.49	0.014	0.007	0.016	0.115	0.064	-	σ_y : 36 kgf/㎟ σ_{max} : 50~63 kgf/㎟

containing 15~20% glycerol at -70℃. The liquid medium was composed of a basal medium and additional nutrients such as sodium thioglycollate (C_2H_3SN; 100 ㎎/ *l*), sodium ascorbate ($C_6H_7NaO_6$ 100 ㎎/ *l*) and $FeSO_4$ 500(㎎/ *l*). The pH of the medium was adjusted to about 7.8 with 1M NaOH and the medium was sterilized at 121℃ for 20 minutes.

2.3 Corrosion measurement

Corrosion potential was measured as a function of exposure time to the liquid medium in the corrosion test cell inoculated with SRB. A negative control was the same condition without the SRB inoculation.

After measuring the corrosion potential, anodic and cathodic polarizations were measured to calculate the corrosion current densities with same test specimens. The measurement equipment was CMS 105 System (Gamry Co., UK). Once the measurement done, photography of SEM was performed after drying for 1 day. Pitting corrosion of surface was observed after the specimen was polished with the sand paper (No. 1000) and degreased with acetone.

3. Results and discussion

Time course of corrosion potential caused by the SRB *Desulfovibrio gigas* (KCTC 2483) was shown in Fig. 2. The corrosion potential gradually decreased until 14 days and then to jump to a noble level in between 14 and 20 days. The first phase of the corrosion potential is most probably due to an electrochemical reaction of cathode and anode of metal surface. Here the biofilms of SRB would be still forming while the corrosion potential dramatically increased due to growth of the biofilms on the surface of test specimen with increasing of SRB population and its activity and the subsequent formation inoculated with the SRB *Desulfovibrio gigas* (KCTC 2483) of corrosion products. A color of medium was changed from gray to black, indicating the presence of iron sulfide (FeS), which was formed through the reduction of sulfate by SRB.

Fig. 3 shows the time course of corrosion potential when the SRB strain was not inoculated. In the beginning the potential rapidly decreased to a lower level and maintained a stable level after 4 days. So it seemed that the stable potential was reflecting a little MIC particularly by SRB. This result was similar to Kikuchi's in terms of the corrosion potential level.[10]

Cathodic and anodic polarizations for the corrosion samples were measured after 40 days' of incubation with the SRB and the results were shown in Fig. 4. It appeared that both mild steel and Normalized steel have a better corrosion resistance than TMCP steel.

Fig. 5 shows cathodic and anodic polarizations for the corrosion samples measured after 40 days' incubation without SRB inoculation. Here the concentration polari-

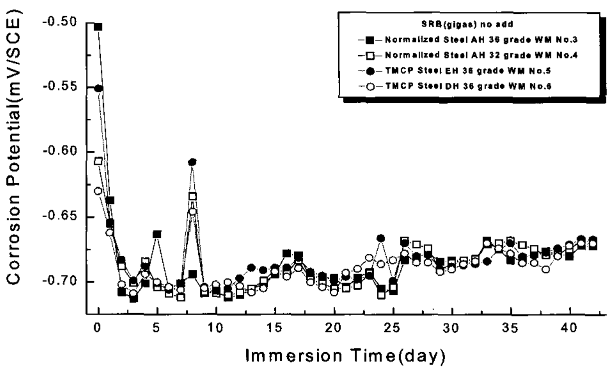

Fig. 3. Time course of corrosion potential in liquid medium without inoculation of the SRB *Desulfovibrio gigas* (KCTC 2483)

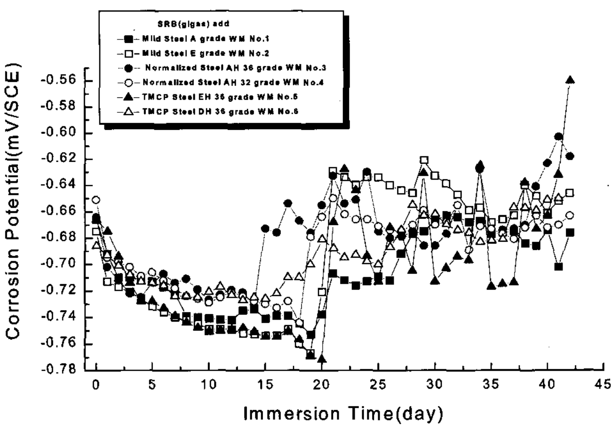

Fig. 2. Time course of corrosion potential in liquid medium

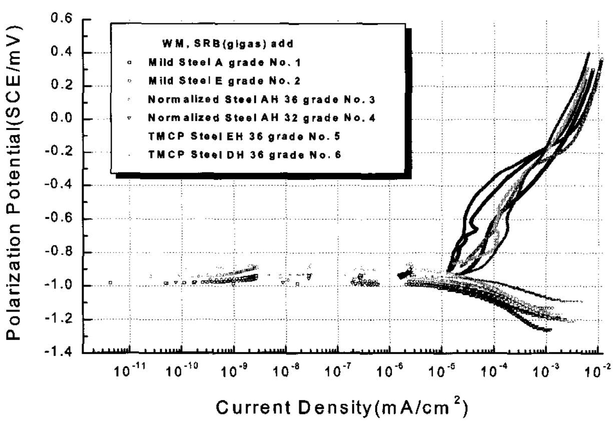

Fig. 4. Cathodic and anodic polarizations curves for various kinds

of steels against the SRB *Desulfovibrio gigas* (KCTC 2483) zation or cathodic passivity may be conducted on the surface in polarization ranging from -0.6 V (SCE) to -1.0 V(SCE) on the cathodic polarization curves. The results showed that the anodic current density rapidly increased in the current density ranging from 10^{-4} A/cm^2 to 10^{-3} A/cm^2. This suggests that a surface film formed with cathodic polarization was cracked in a short time, and the anodic current density increased promptly.

Values of the corrosion current densities supporting Fig. 4 and Fig. 5 were based upon the Stern-Geary method and Tafel extrapolation method and are shown in Table 3 and in Fig. 6. Corrosion current densities obtained from

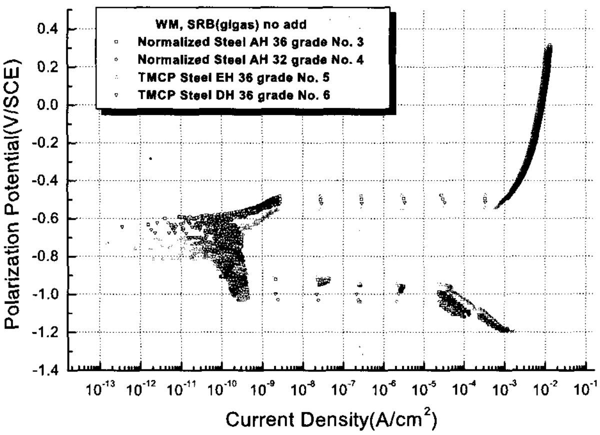

Fig. 5. Polarization curves of Normalized and TMCP steels without the inoculation of *Desulfovibrio gigas* (KCTC 2483)

Tafel extrapolation method showed the higher values than those of Stern-Geary method. Moreover, the corrosion current densities in the presence of the SRB were higher than in the absence of SRB. By the way there have been many observations about the corrosion-causing microorganisms[11)-16)] and SRB appear to be the most dominant and critical bacteria associated with the corrosion. SRB require anaerobic conditions for growth, but many strains can stay alive for a long period in aerobic conditions, ready for activation when conditions become favorable. However, this makes the SRB the most notorious and harmful of the microorganisms known to enhance corrosion. The mechanism by which the anaerobic SRB can facilitate corrosion of iron and carbon steel is uncertain, but a recent review[17)] gives some important facts and the theory:

Anodic reaction : $4Fe \rightarrow 4Fe^{2+} + 8e^-$

Cathodic reaction : 1. $8H_2O \rightarrow 8H^+ + 8OH^-$

2. $8H^+ + 8e^- \rightarrow 8H$

3. $SO^{2-}_4 \rightarrow S^{2-} + 4O$

4. $4O + 8H \rightarrow 4H_2O$

5. $Fe^{2+} + S^{2-} \rightarrow FeS$

6. $3\ Fe^{2+} + 6OH^- \rightarrow 3Fe(OH)_2$

Summarization reaction : $4Fe + 4H_2O + SO^{2-}_4 \rightarrow 3Fe(OH)_2 + FeS + 2OH^-$

SRB reduce sulfate ions to sulfide as shown in the cathodic reaction 3 above, so that a nascent hydrogen, H can easily react with oxygen, O as shown in the above

Table 3. The data of corrosion current densities obtained by both Stern-Geary and Tafel extrapolation methods for Mild, Normalized, and TMCP steels with and without the inoculation of the SRB *Desulfovibrio gigas* (KCTC 2483).

Item Specimen		Icorr(A/㎠) Stern-Geary	Tafel Extrapolation	E_{corr}(㎷)	Beta C (㎷/Decade)	Beta A (㎷/Decade)	R_p (Ω ㎠)
Mild Steel A grade No. 1	Inoculation	2.234×10^{-10}	1.875×10^{-5}	-968.4	12.0	20.4	1.470×10^{7}
	No inocul.						
Mild Steel E Grade No. 2	Inoculation	3.780×10^{-10}	2.571×10^{-5}	-958.2	5.1	13.7	4.291×10^{6}
	No inocul.						
Normalized Steel AH 36 grade No. 3	Inoculation	9.274×10^{-12}	2.334×10^{-5}	-956.1	1.0	18.2	4.292×10^{7}
	No inocul.		1.623×10^{-10}				
Normalized Steel AH 32 grade No. 4	Inoculation	3.050×10^{-11}	2.625×10^{-5}	-968.3	4.8	5.5	3.644×10^{7}
	No inocul.		2.663×10^{-10}				
TMCP Steel EH 36 grade No. 5	Inoculation	7.009×10^{-10}	2.575×10^{-5}	-882.1	13.1	7.3	2.901×10^{6}
	No inocul.		1.844×10^{-10}				
TMCP Steel DH 36 grade No. 6	Inoculation	2.451×10^{-10}	3.857×10^{-5}	-9.339	3.0	2.5	2.431×10^{6}
	No inocul.		2.084×10^{-10}				

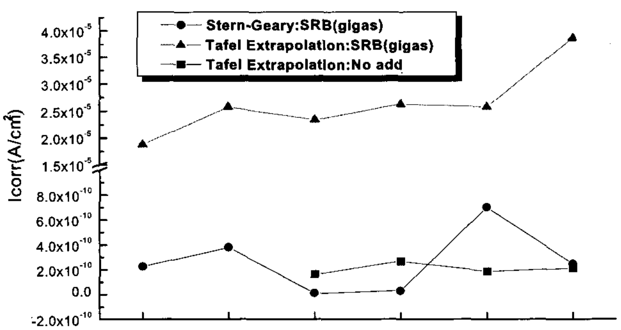

Fig. 6. Comparative analysis of corrosion current densities measured by Tafel and Stern-Geary methods for Mild, Normalized and TMCP steels in the presence and absence of the SRB *Desulfovibrio gigas* (KCTC 2483).

reaction 4. Consequently the cathodic reaction 2 increases, enhancing the subsequent the cathodic reaction 4 which is accelerated by reaction 3 caused by SRB. Eventually accelerated cathodic reaction 2 can be assumed to increase anodic reaction with increasing corrosion current density. It can be, therefore, concluded that the SRB can accelerate corrosion rates.

Experimental results discussed so far is considered to be rather a qualitative investigation. So it is likely that more researches must be done about MIC by SRB with a more quantitative way.

Plate 1 shows corroded surface of test specimens after 40 days' incubation with the SRB (strain KMU-2) isolated from a crude oil sample. Here we could observe the pitting corrosions due to accelerated cathodic reaction and concentration cell of oxygen by SRB. However, in Plate 2 the pitting corrosion was not observed because there might be no cathodic reaction acceleration as well as concentration cell forming. So it is quite evident that SRB could be involved in enhancing the corrosion (particularly a pitting corrosion) and these results echoed with some other previous reports,[10),18)] which also showed pitting corrosions of stainless steel and copper steel with SRB.

Plate 3 shows the SEM photographs of SRB growing on the surface of a steel and the morphology of SRB used in this study was also similar to that of other results.[10),18)]

4. Conclusion

In absence of SRB, corrosion potential shifted to a low level in the beginning and then maintained a stable level later on. However the corrosion potential shifted to lower

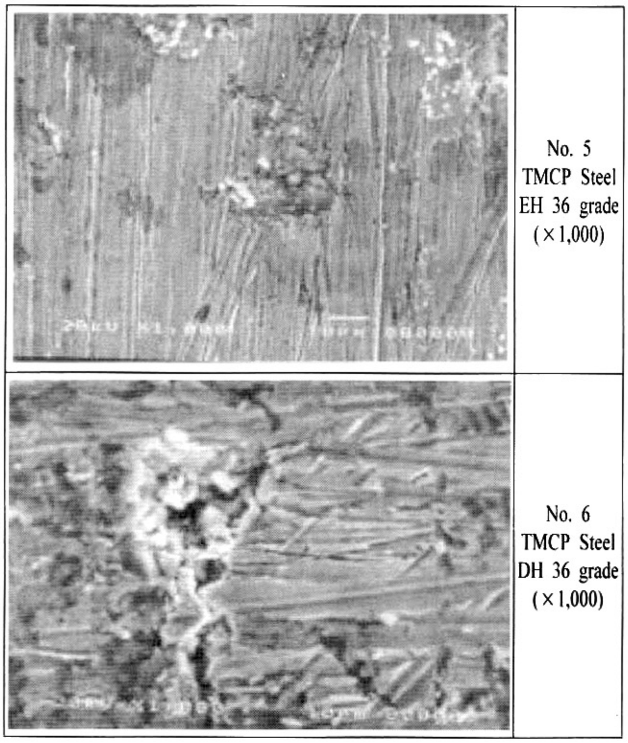

Plate 1. SEM photographs of polished surface for test specimens after 40 days' incubation with the SRB strain KMU-2 isolated form a crude oil sample

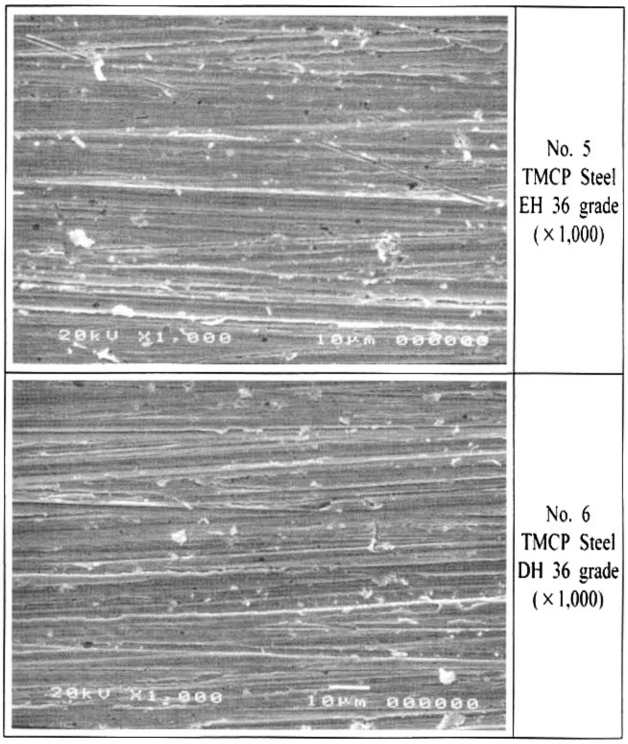

Plate 2. SEM photographs of polished surface for test specimens after 40 days without the SRB strain KMU-2 inoculation.

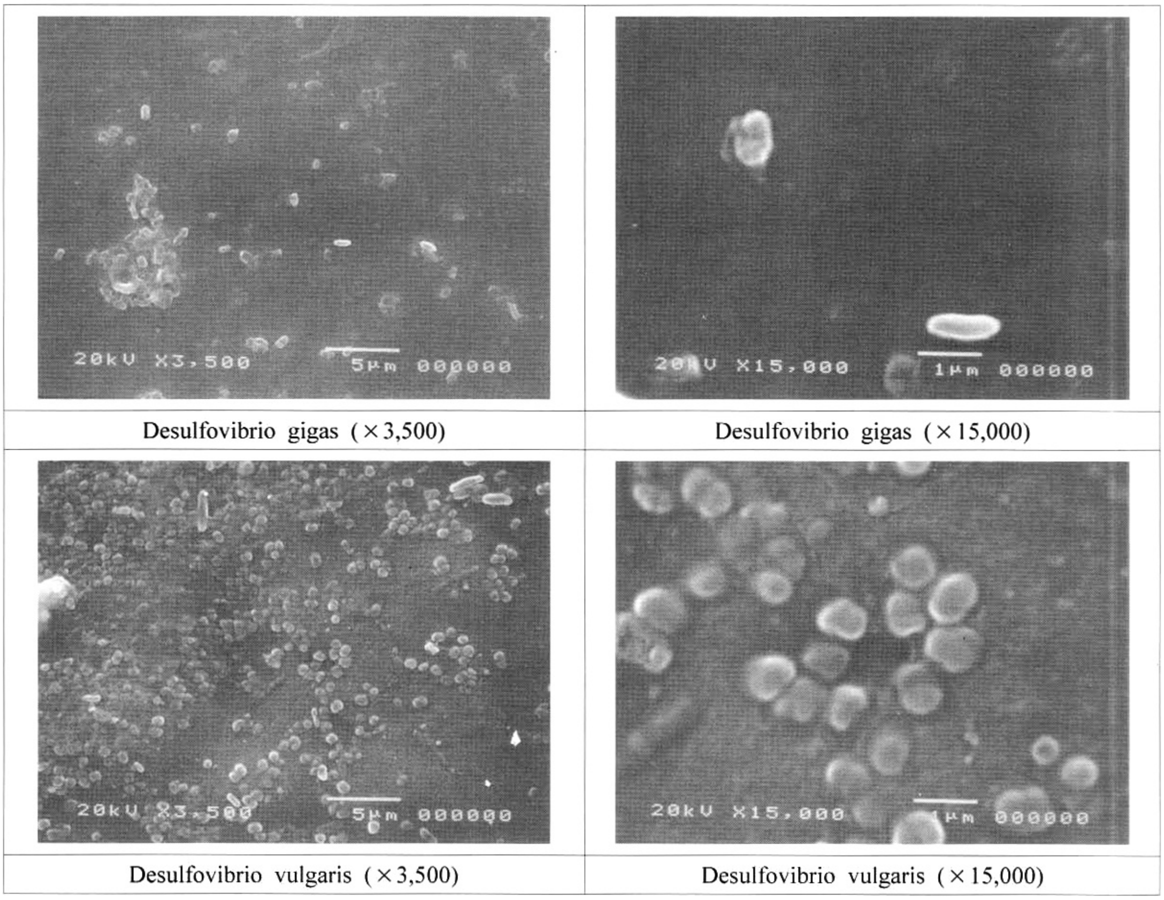

Plate 3. SEM photographs of SRB of *Desulfovibrio gigas* and *Desulfovibrio vulgaris* KCTC 2483 obtained from the Korean Collection for Type Cultures, Korea Institute of Bioscience and Biotechnology

range in the beginning with the SRB presence, but after 14 to 20 days' incubation, the corrosion potential changed to a noble level again, indicating MIC caused by the SRB.

Corrosion current density in the presence of SRB was higher than that in absence of SRB. Furthermore, a pitting corrosion was observed in the SRB growing medium while the control did not show any such phenomenon. Normalized steel had a better corrosion resistance than the TMCP steel. It appeared that there were some differences between polarization curves depending on the presence or absence of SRB in the corrosion test cell.

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