Bull. Mar. Sci & Tech 11(1), 2002
Research Institute of Marine Science and Technology
Korea Maritime University

An Electrochemical Study on the Microbiological Influenced Corrosion of Steels Sulfate-Reducing Bacteria

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ABSTRACT

We have investigated the differences between the geneal corrosion and microbiologicall influenced corrosion (MIC) of a steel in terms of electrochemical behavior and surface phenomena. Corrosion potential of a steel in medium solution without SRB (Sulphate Reducing Bacteria) shifted to a low direction continuously as a function of submerging time.

The potential caused by MIC with SRB shifted to a noble direction after 20days' incubation, indicating the growth of SRB biofilm on the test metal specimens and a formation of corrosion product. In addition, the color of medium inoculated with SRB changed from grey to black., the color change was 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 a steel in MIC were higher than those is the absence of SRB. This is probably because SRB caused be associated with the increasing corrosion rates through increasing cathodic reaction which caused the reducing sulfate to sulphide as well as formation of an oxygen concentration cell. The pitting corrosion was also observed in the of SRB inoculated medium.

Key words : Microbiological Influenced Corrosion, Corrosion Potential, Sulphate Reducing Bacteria, biofilm, Pitting Corrosion

1. INTRODUCTION

Although it is true that qualitative research results as to corrosion associated with a microorganism was known to from about 100 years ago, corrosion study associated with microorganism was carried out predominantly from 1980 because corrosion damage was considered as one of factors causing by bacteria. However for the first time R.H.Gaines[1] suggested that corrosion of both the inner and outer side of a water pipe was influenced with sulfide oxidizing bacteria and Iron-oxidizing bacteria .

Recently with rapid development of industrial society all kinds of structural steels were presented with severe corrosive environments, therefore corrosion resistance of a steel was appeared with an important content in terms of both economical view and industrial safety view. In spite of that, unexpected accident causing by corrosion of a structure was often happened, for example water of pipe line was leaked due to corrosion of welded area of stainless steel pipe inspected completely for less than several months [2~4], and unexpected severe pitting corrosion in cargo oil tank bottom plating was observed [5]. In addition to study results on corrosion damage of fuel oil tank in aircraft as well as the abnormal corrosion of weld metal area of stainless steel was reported [6~7].

A series of corrosion accidents mentioned above is not reasonable to be considered with conventional corrosion based on electrochemical theory in a simple concept, eventually it was 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 were often happened and the amounts of damage is over several billion dollars as well [8~9].

In this study, the susceptibility of MIC(Microbiological Influenced Corrosion) by SRB(Sulphate Reducing Bacteria) of TMCP(Thermo Mechanical Control _Process) steel, Normalized steel and conventional Mild steel was investigated based on the electrochemical view. Therefore it suggested that this study may be helpful to give the comparison of MIC susceptibility about some kinds of steels but also to examine the difference of polarization behavior according to MIC or not.

2. EXPERIMENTAL

2.1 Corrosion cell and Test specimen

After the surface of test specimen was polished with sand paper, No. 1000 and degreased with acetone, it was insulated with epoxy coating except 1㎠ area for measuring experiment. And after test specimens for measuring corrosion potential, polarization curves and for photographing SEM put into the beaker of 500㎖ capacity, both liquid medium solution 300 ㎖ and SRB medium solution, 30㎖ injected into the beaker. On the other hand the upper part of beaker was sealed with a special plastic cover which was made of inlet & outlet hole for injection Nitrogen gas and inserting hole for salt bridge of reference electrode. And the experimental apparatus was shown in Fig. 1 and Table 1 showed chemical composition of test specimens.

2.2 Liquid medium solution and SRB

SRB used in this study was obtained from Genetic Resource Center. And it's detail was Desulfovibrio gigas(KCTC No. 2483). Gigas bacteria was protected in liquid medium added with 15~20% Glycerol. And maintained with room temperature, at -70℃. And liquid medium was separated with basal medium and complete medium. And in the first place basal medium solution was made, after that complete medium solution was made with basal medium solution added with sodium thiogly collate(C_2H_3SNa) 100(㎎/ℓ), sodium ascorbate($C_6H_7NaO_6$) 100(㎎/ℓ) and $FeSO_4$ 500(㎎/ℓ). And pH adjusted about 7.8 with 1M NaOH and sterilized for 20 minutes in room temperature at 121℃.

Table 1 Chemical composition(wt%) of test specimens

Item	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	-	σy : 24kgf/㎟
mild steel, E grade	0.105	0.178	1.12	0.019	0.005	0.007	0.015	0.003	-	σy : 24kgf/㎟
Normalized steel, AH36	0.110	0.288	1.34	0.011	0.005	0.007	0.011	0.005	-	σy : 36kgf/㎟ σmax:50~63kgf/㎟
normalized steel, AH32	0.136	0.158	1.05	0.013	0.007	0.006	0.010	0.005	-	σy : 32kgf/㎟ σmax:48~60kgf/㎟
TMCP steel, EH36	0.148	0.457	1.46	0.017	0.005	0.009	0.020	0.037	0.028	σy : 36kgf/㎟ σmax:50~63kgf/㎟
TMCP steel, DH36	0.173	0.435	1.49	0.014	0.007	0.016	0.115	0.064	-	σy : 36kgf/㎟ σmax:50~63kgf/㎟

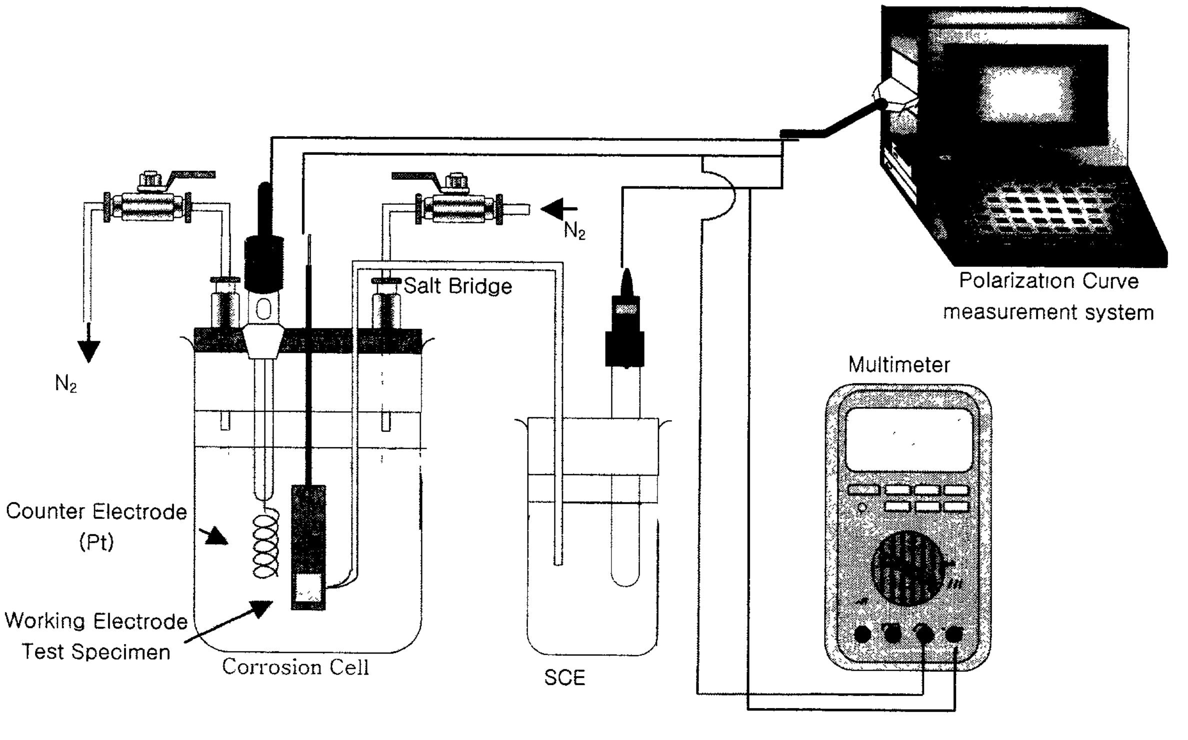


Fig. 1 Schematic Diagram of experimental apparatus

2.3 Measuring method

Corrosion potential was measured as a function of exposed time with SRB add or not during deaerating with N_2 gas injection into beaker cell.

After measuring corrosion potential, anodic and cathodic polarization curves was measured for calculating corrosion current density with same test specimens and experimental equipment for measurement was CMS 105 system of Gamry Company and photographed SEM after dried in dryer for 1 day. And pitting corrosion of surface was observed with high multiple photograph after the specimen was polished with sand paper, No. 1000 and degreased with acetone.

3. RESULTS AND DISCUSSION

The results of variation of corrosion potential as a function of exposed time in case of SRB add was shown in Fig. 2, as known in Fig. 2 in the beginning submerged the corrosion potential shifted to lower direction, however corrosion potential jumped to noble direction after submerged between from 14 days to 20 days. It is suggested that in the beginning submerged corrosion potential shifted to low direction because not by affect of MIC but with the conventional phenomenon of general corrosion based on the electrochemical reaction of cathode and anode of metal surface and shifting to noble direction again is due to forming of corrosion products and growth of biofilm on the surface of test specimen with increasing of SRB and its activity. And the color of medium solution was changed from grey to black by creating iron sulphide(FeS), which was formed by reducing sulphate to sulphide by SRB.

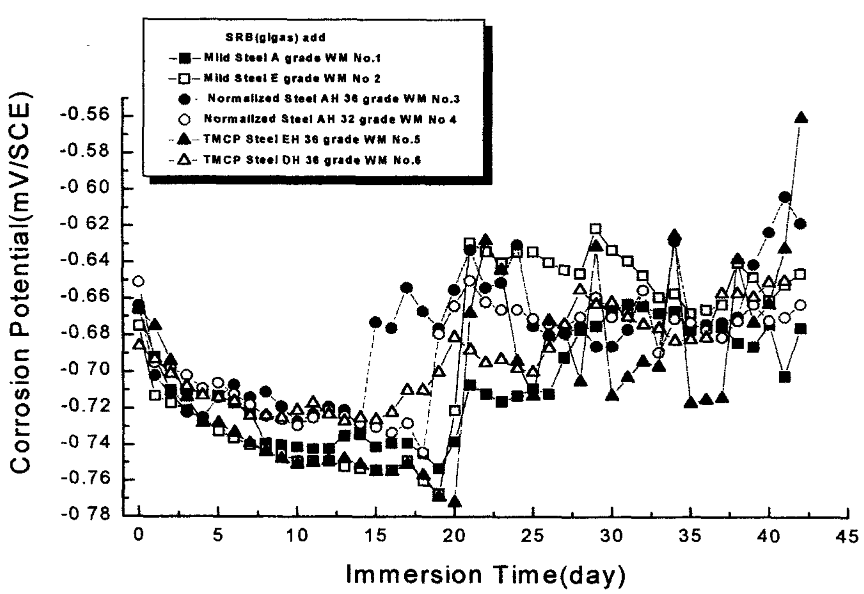


Fig. 2 Variation of corrosion potential in complete medium solution with SRB(gigas) addition

Fig. 3 shows variation of corrosion potential as a function of exposed time in case of without SRB add, from these results, it can be known that in the beginning corrosion potential shifted to low direction and maintained stable condition, so it seems that corrosion potential indicating stable condition means that the influence of MIC was not revealed due to free SRB add. Furthermore we could know that the results as for the corrosion potential measurement was similar to Kikuchi's test results [10].

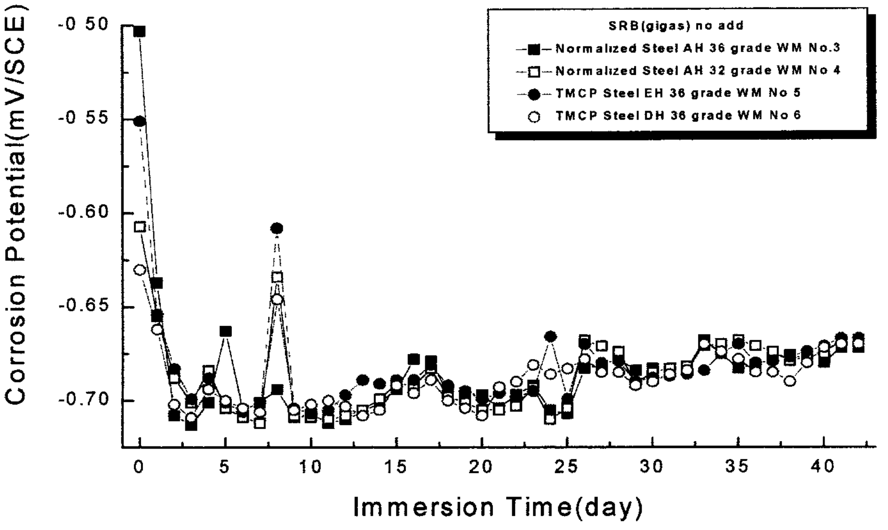


Fig. 3 Variation of corrosion potential in complete medium solution without SRB(gigas) addition

A Cathodic and anodic polarization curves were measured after submerged 40 days with SRB add was shown in Fig. 4. And it seems that both mild steel and Normalized steel have a little good corrosion resistance than TMCP steel.

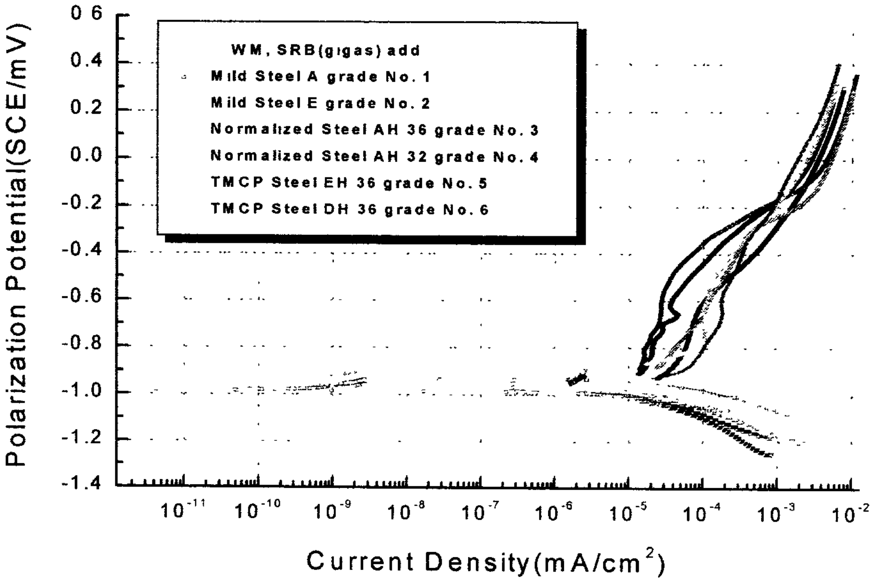


Fig. 4 Polarization curves of all kind of steels with SRB(gigas) add solution

Fig. 5 shows a cathodic and anodic polarization curves measured after submerged 40 days without SRB add. As shown in Fig.5 concentration polarization or cathodic passivity may be conducted on the surface in polarization of from –0.6V (SCE) to –1.0V(SCE) on the cathodic polarization curves however it can be known that anodic current density was rapidly increased in the area from 10^{-4}A/㎠ to 10^{-3}A/㎠ on the anodic polarization curves, it is suggested that surface film formed with cathodic polarization was cracked in a short time, so that anodic current density was increased promptly.

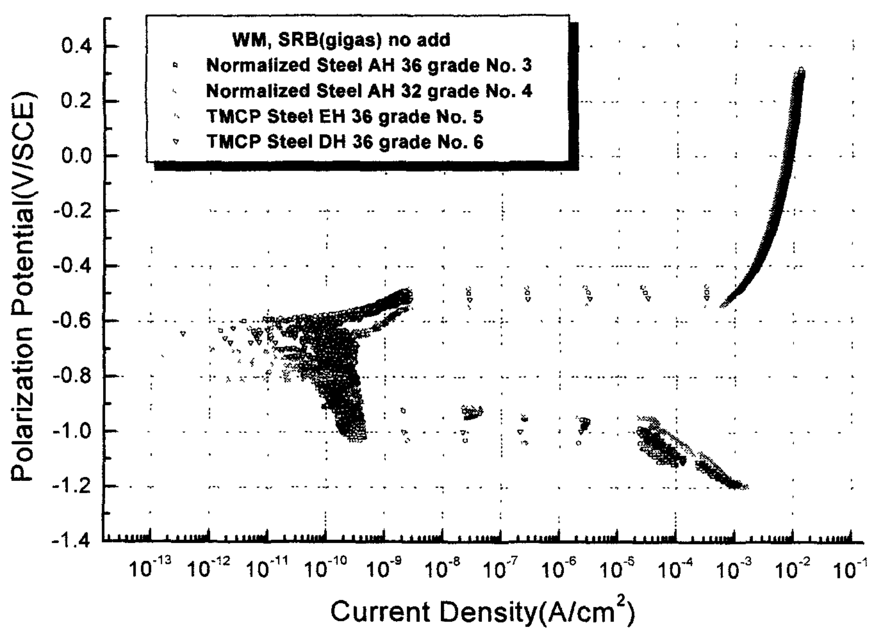


Fig. 5 Polarization curves of Normalized and TMCP steels with SRB(gigas) no add solution

The corrosion current densities obtained from Fig. 4 and Fig. 5 based on Stern-Geary method and Tafel extrapolation method is shown in Table 3 and in Fig. 6. Corrosion current density obtained from Tafel extrapolation method showed the bigger value than that of Stern-Geary method and corrosion current density with SRB add was higher than that of SRB no add. On the other hand there are many opinions about corrosion associated microorganism [11~16] and SRB are thought to be the dominant and most important bacteria associated with corrosion and SRB require anaerobic conditions for growth, many strains can stay alive for long periods in aerobic condition, ready for activation when conditions become favorable. However SRB are easily the most notorious and harmful of the microorganisms known to enhance corrosion. The mechanism by which anaerobic SRB accomplish an increase in corrosion of iron and carbon steel is uncertain, but a recent review [17] gives some important facts and in 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 : $4Fe + 4H_2O + SO^{2-}_{4} \rightarrow 3Fe(OH)_2 + FeS + 2OH^{-}$

Table 3 The data of corrosion current densities obtained by both Stern-Geary and Tafel extrapolation methods for Mild, Normalized, and TMCP steels with SRB(gigas) add or not

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

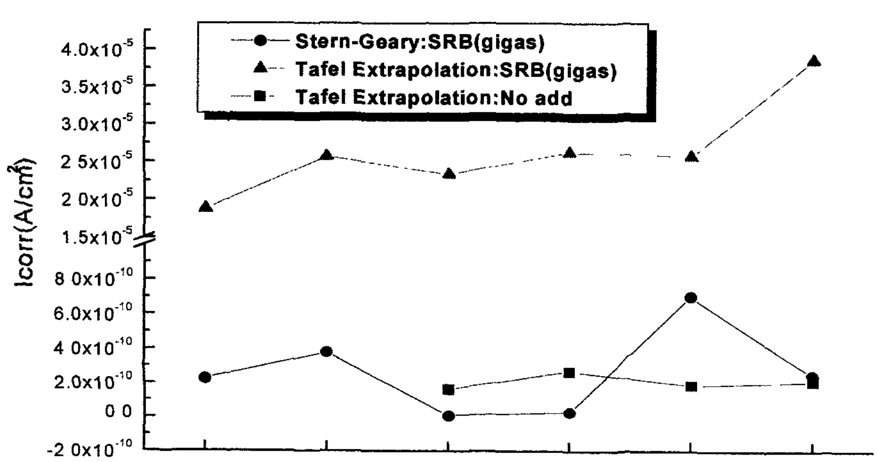


Fig. 6 Variation of corrosion current density between Mild, Normalized and TMCP steels with SRB(gigas) add or not

SRB reduce sulfate ion to sulphide as shown above cathodic reaction No.3, so that nascent hydrogen, H can easily react with oxygen, O as shown above No.4 reaction. Consequently cathodic reaction No.2 is increased with increasing cathodic reaction No.4 which is accelerated by No.3 reaction caused by SRB. Eventually accelerated cathodic reaction No.2 can be considered to increase anodic reaction with increasing corrosion current density. Therefore it can be concluded that existence of SRB can accelerate corrosion rate more than no existence of SRB.

Experimental results discussed until now is considered to be a qualitative investigation conventionally, so it seems that more research must be done about MIC by SRB with a more precise and quantitative way.

Photo. 1 shows corroded surface of test specimen after submerged 40 days with SRB add, as shown in Photo. 1 we can observed the pitting corrosion due to accelerated cathodic reaction and concentration cell of oxygen by SRB however in Photo. 2 it can not be observed the pitting corrosion because it may be no cathodic reaction acceleration as well as concentration cell forming, it is very well evident that SRB may be performed to enhance corrosion especially pitting corrosion and these results correspond with some other reports[10,18], which also indicate pitting corrosion to stainless steel and copper steel with SRB.

Photo. 3 shows the shape of SEM photographs of SRB obtained from Genetric Resources Center, and the shape of SRB used in this study approximately was also similar to other results examined about MIC by using SRB[10,18].

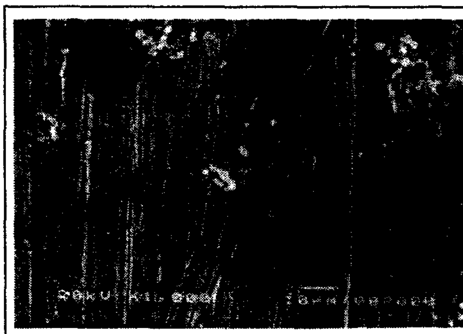
	No. 5 TMCP Steel EH 36 grade (×1,000)
	No. 6 TMCP Steel DH 36 grade (×1,000)

Photo. 1 SEM photographs of polished surface for test specimens after 40 days with SRB extracted form crude oil

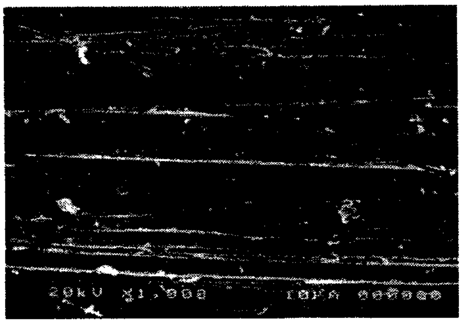
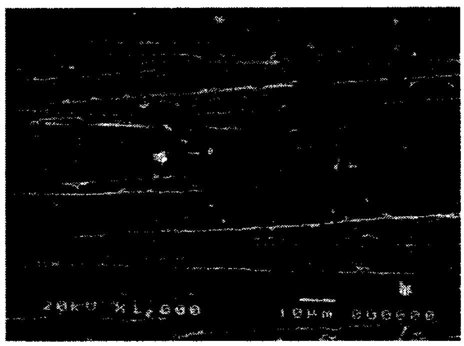
	No. 5 TMCP Steel EH 36 grade (×1,000)
	No. 6 TMCP Steel DH 36 grade (×1,000)

Photo. 2 SEM photographs of polished surface for test specimens after 40 days without SRB extracted form crude oil

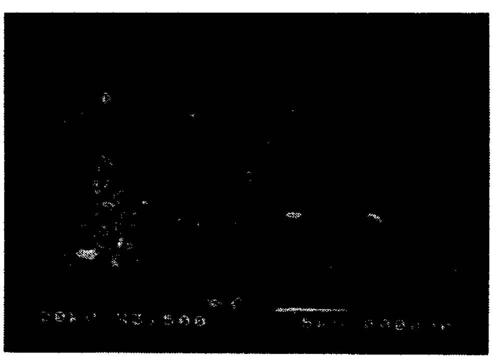
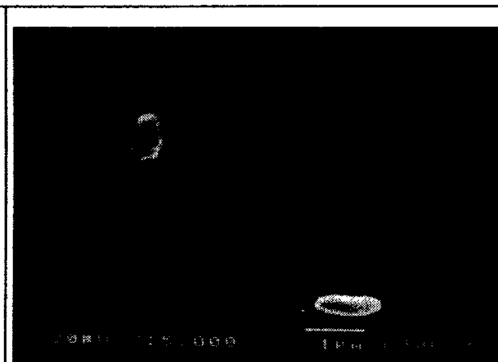
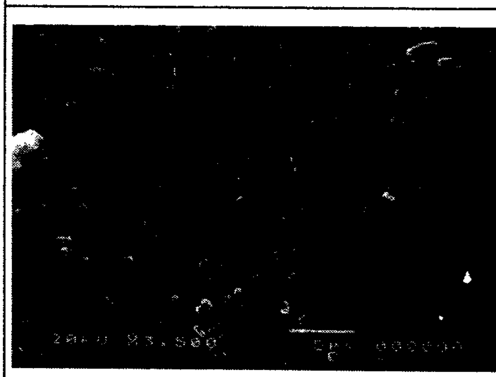
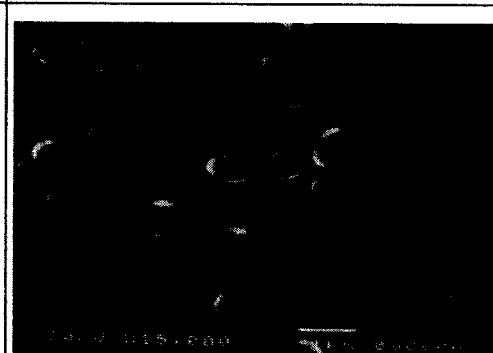
	
Desulfovibrio gigas(×3,500)	**Desulfovibrio gigas(×15,000)**
	
Desulfovibrio vulgaris(×3,500)	**Desulfovibrio vulgaris(×15,000)**

Photo. 3 SEM photographs of SRB of Desulfovibrio gigas and Vulgaris purchased from genetic resources center

4. CONCLUSION

In case of SRB no add, corrosion potential shifted to low direction in the beginning and after that maintained stable condition continuously. However corrosion potential shifted to low direction in the beginning with SRB add but after submerged from 14 days to 20 days, corrosion potential shifted to noble direction again, which is considered to be one of the important factors indicating influence of MIC by SRB.

Corrosion current density with SRB add was higher than that of SRB no add furthermore pitting corrosion could be observed in case of SRB add while could not be observed in SRB free condition. And Normalized steel had a little good corrosion resistance than TMCP steel. It appeared that there were some difference on the shape of polarization curves according to SRB add or free.

5. REFERENCES

1. M. Yama, in *Proceedings of the 100th Corrosion & Corrosion Control Institute Symposium*, 1994, P. 55(in Japanese).
2. M. Yama etal, in *Proceedings of the 36th Corrosion & Corrosion Control Institute Symposium,* 1989, P. 1449(in Japanese).
3. N. Mura, in *Proceedings of the 89th Corrosion & Corrosion Control Institute Symposium,* 1992, P. 49(in Japanese).
4. W. Sin, *Engineering Department of Hoka College*, 1999, P. 5.
5. *Oil Companies International Marine Forum*, Factors Influencing Accelerated Corrosion of Caryo Oil Tank, Sept 1997, P. 1
6. A. Hagenauer, R. Hilpert and T. Hack, *Week stoffe und Korrosion* 355, 45(1994).
7. K. R. Sreekumari, M. Ozawa, Y. Kikuchi, *IDJI. International*, 54, 40(2000).
8. *Proc. 10th International Biodeferioration and Biodegradation Symposium*, Hamburg, September, 1996, P. 4.
9. G. J. Licina, *Source Book for Microbiologically Influenced Corrosion in Nuclear Power Plants*, Electric Power Research Institute Report, 1998, P. 35
10. Y. Kikuchi, K.Tohomoto, M. Ozawa, T. kanamaru, *Corrosion* 199 Paper No. 170
11. Y. Toyuo, *Corrosion Engineering & Corrosion Technology*, Corona(Eds), 1975, P. 361(in Japanese)
12. S. Hyra , *Journal of the Japan Institute of Metals*, 135, 9(1970)
13. J. W. West, (S. Nota Tran.) : *Corrosion & Oxide Industry Publication*, 1990, P. 104
14. J.You, *Journal of the Japan Institute of Metals*, 775, 58(1994)
15. *A High Molecule Society, A Society for the Research of Bio ·High Molecule*, 1988, P. 189
16. Y. Kikuchi, K. Tohomoto, *ZAIRYO-TO-KANKYO*, 467, 47(1998)
17. A. K. Tiller, *Biologically Induced Corrosion*, S. C. Dexter, ed., NACE, Houston, P. 8, 1986
18. Y. Kikuchi, Technical Explanation, Joining and welding Research Institute, Osaka University, 119, 7(1999)