Review of Microbiologically Influenced Corrsoion (MIC) of Metal Welds in Japan

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Abstract

In recent years, Microbiologically Influenced Corrosion(MIC) of industrial materials and its welds have been identified as one of the serious problems in the chemical process plant, energy planet and water supply systems. In Japan, there are many misunderstandings about MIC on the welds and only limited amounts of information exist on MIC and biodeterioration of metals and their weld joints.

This paper attempts to outline what information is available, describing the nature of MIC, case history in Japan and current laboratory-scale test results.

KEY WORDS: (Corrosion) (Welds) (Microbially) (Corrosion)

1. Introduction

The problem of the performance of industrial materials and products being impaired by micro-organisms (moulds) is certainly not new and has long been empirically known. Equally well recognized is the long history enjoyed by technologies exploiting the beneficial effects of microorganisms . A vast number of micro-organisms exists, and their actions also differ very widely. More recently, corrosion in which micro-organisms are implicated(microbiologically influenced corrosion (MIC) has engaged special attention in industrial technology.

Corrosion attributed to MIC has affected chemical plants, offshore structures , power plants, concrete structures, etc, and the damage caused by MIC in some situations cannot be ignored. The reason why MIC has so far been largely neglected by corrosion research techniques possessing much improved accuracy may well be that the mechanisms are far from being properly understood and that it is necessary to clarify the interaction between materials and micro-organisms.

Some incidents in which metal welds have been affected by extremely fast corrosion(e.g. rates estimated at around 0.57mm/S(18mm/year)in SUS304)have been reported together with problems of new weld-related corrosion defects.[1-2] This problem concerns impairment of materials and corrosion induced by micro-organisms adhering to welds. Regardless of the defects produced by corrosion, MIC-related effects are essentially poorly understood, with the result that they are in many cases mistaken for welding defects, such as poor bead profile, cracking , etc, in welding fabrication and treated by repair welding, while the true causes remain a msystery. Although it is impirically known that the involvement of micro-organisms is largely ignored problem and that routine remedial treatment can be used to make good any damages, the lack of any general awareness that metal welds may in some cases be heavily corroded by micro-organisms may be due to the fact that most expert welding technologists, reseraches, etc, do not have a sufficiently detailed grasp of the problem. In Japan, examples of the problem are very poorly documented. This paper attempts to outline what information is available, describing the nature of MIC as well as current research efforts.

2. Microbiologically influenced corrosion of metal welds Do micro-organisms like welds?

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The nature of MIC and some examples are presented below. The characteristics of MIC include the following;

1. A fast corrosion rate. Regardless of the fact that , as noted above , metals represent a relatively mild environment, examples of corrosion being initiated in equipment free from any flowing water, in pipelines where hydraulic pressure tests have been completed and some purged water is retained inside, etc, suggest an extremely fast estimated corrosion rate.
2.When the cross-sectional shape of the corrosion pits is examined, they are in many cases found to be pot-shaped, i.e. They have small inlets and an expanded interior which again narrows off.
3. Corrosion initiation sites reveal lumps of rust , which are regarded as being the metabolic products of micro-organisms. The corrosion pits are observed just under or very near them. The color of these lumps of rust varies depending on the micro-organisms implicated in the material and may be red, black , or yellow. Their morphology also varies, not being solid at the start of formation, but becoming solid with the lapse of time.

Some examples affecting SUS304 stainless steel are given below . **Figure 1** shows a cross-sectional microphotograph and structural photograph of a weld. The corrosion shown here concerns the welded joints in a water storage tank produced from 4mm thick plate. The water represents a neutral environment at ambient temperature. Both the weld metal and HAZ are attacked as though gouged out. The corrosion morphology confirms the attack as being MIC.

Figure 2 shows a SEM microphotograph of a corrosion pit. The view shown here is after removal of a lump of rust in the 308 weld metal.

Selective corrosion is found to occur. There are some traces of corrosion suggesting that the γ phase is preferentially attacked. As time elapses, the retained α phase is also corroded, with development into perforating pits. In contrast to this case, another examples affecting the retained α phase has also been reported.[3] The corrosion process here is considered to be controlled by the material, the implicated micro-organisms, and the environmental conditions. It appears that, far from being limited to surface welds, micro-organisms have been shown to be quantitatively implicated in corrosion of pipes buried in the soil[4]. According to the results presented in this paper, buried steel pipes normally form iron oxides on their surface as time passes and become covered in rust, whose effect is gradually to inhibit further corrosion. Micro-organisms, however, occur in the soil, and , if they become involved in metal corrosion, the composition of the rust products changes, with the result that steel pipes may sustain perforating corrosion pits.

Some another case affecting SUS304 stainless steel pipeline for oil trasport is descrived.(Offered by Prof. Itomura, Rykyuu University) This was reported in 1995. In this case, it was used city water for pressure tightess test to welded pipes. After testing, city water was retained in the tested stainless steel pipings. Leaking was found from several welded joints. The failures in weldd joints (welded metal, HAZ and base metal) occured with in apraximately 4 months from the start up of the plant.

Figure 3-(I) shows a surface of base metal. The large corrosion holes were recognized. A cross-section of the large corrosion hole was shown in Figure 3-(I)A and B. The corrosion hole in the weld metal is shown in Figure 3-(II) arrow. Cross section of weld metal was shown in Figure3-(III).(arrow). Both the weld metal and HAZ are attacked as though gouged out. The corrosion morphology confirms the attack as sing MIC.
The anticipative leaking troubles due to MIC are collecting by the author's research group. Failure analysis and laboratory-scale simulation tests are undertaking.

At the presetn time, 7 ~8 cases are reported. 304 and 316 stainless steel were used. Diagnostic water was river, ground (mixed sea water) and city water. The results will be reported later.

NACE International have recently published a number of excellent papers explaining MIC together with numerous examples and a rich array of color photographs.[5,6]

These papers given an extremely helpful insight into MIC and provide good reference material on the subject.

The papers cited above give numerous examples of MIC affecting welds and tend at a glance to give the impression that corrosion defects occur not only in welds, but also in the base metal apart from welds. It is questioned why are welds so heavily affected and whether micro-organisms might not actually prefer welds. Although numerous tests have so far been conducted, the conclusions are unclear. The weld metal surface is far from being uniform and never smooth, it may bear some retained ripple lines and slag, and it may be covered with an oxide film. The HAZ is heated to a high temperature and forms irregularities through an extremely thin surface layer being melted by the arc. Under such surface conditions , micro-organisms can easily adhere and substances suspended in water are also precipitated and accumulate, thus forming an environment in which micro-organisms may thrive and

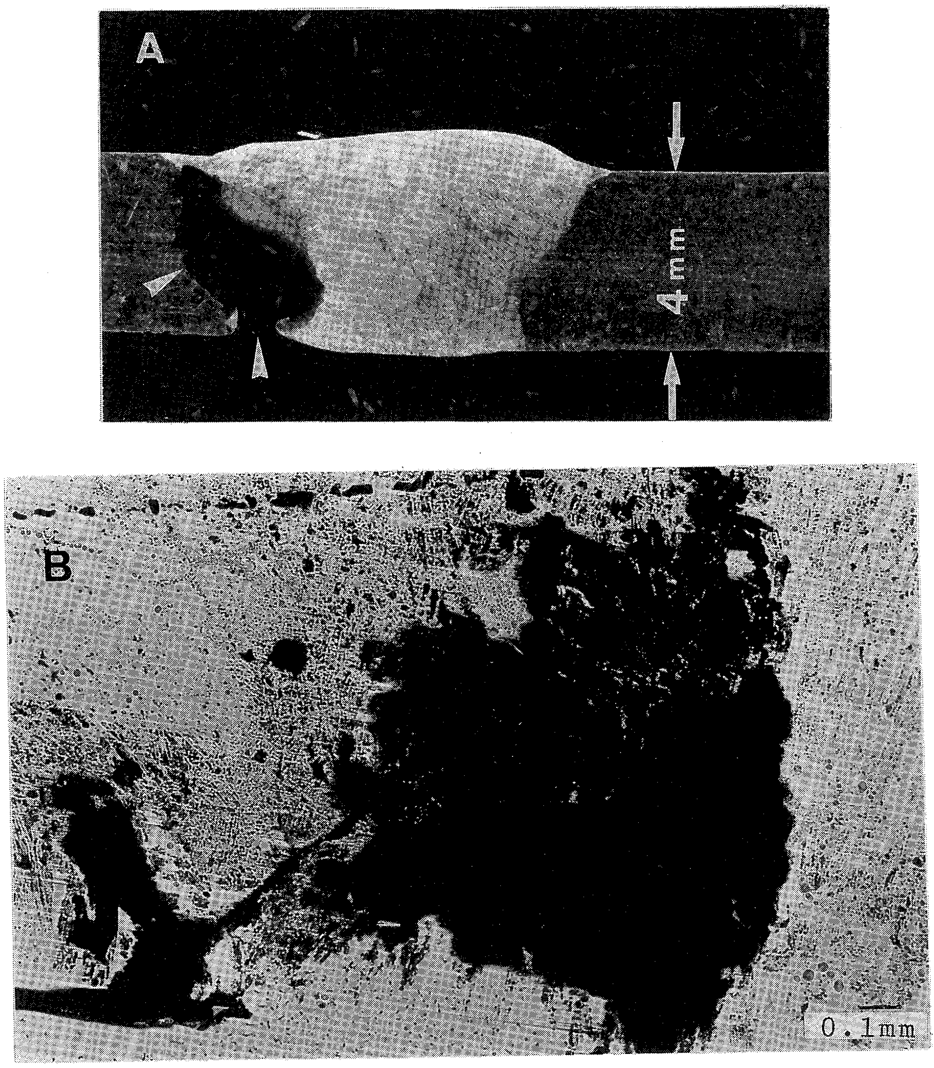


Fig.1 Examples of weld corrosion due to MIC(A:Microphotograph, B:Structure of Corroded zone)

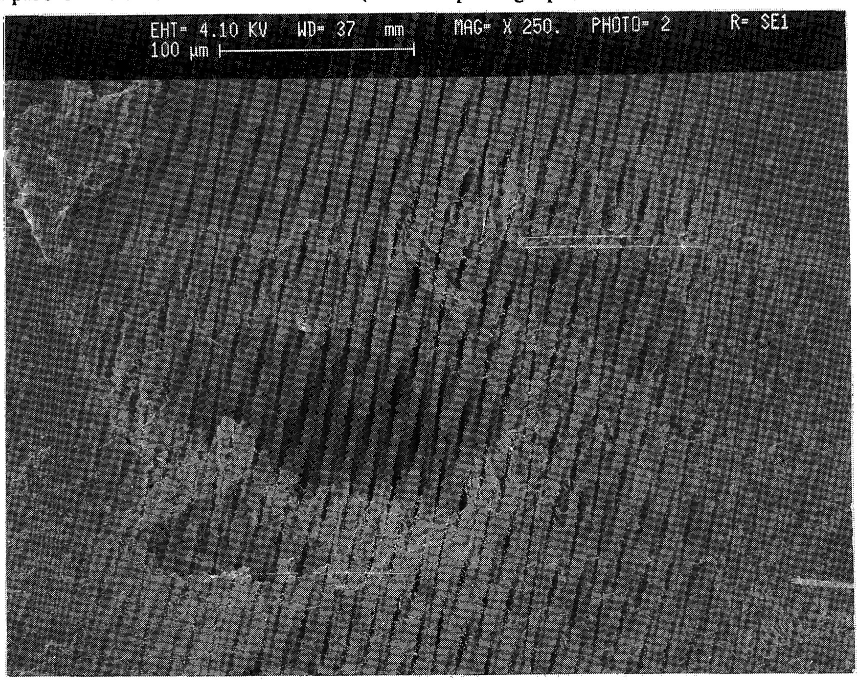


Fig.2 MIC corrosion pit in 308 weld metal. The phase γ is preferentially attacked, leaving the α phase. (Acknowledgments :Prof. C.Lundin and Dr. J Danko, University of Tennessee Knoxville, USA)

proliferate. This environment is akin to the man-made gathering places for fish used for breeding fish at sea. The as-welded joints also readily acquire protuberances and may possibly act as sites where liquid flow in non-uniform or stagnant conditions exists, so that micro-organisms and suspended substances can accumulate and micro-organisms multiply.

Buchanan[7] performed an investigation to examine the relationship with MIC initiation behavior when these weld metal surface conditions are changed. The results obtained suggest that MIC initiation susceptibility decreases in an as-welded, ground, and polished sequence. **Figure 4** gives a typical example of these results relating to 308 weld metal tested with A6F bacteria solution(considered to contain Gram-negative, aerobic, and anaerobic bacteria). The specimens finished with #600 SiC paper showed a sharply reduced corrosion potential after being kept immersed in the solution for 10hr, and numerous pits were found on the specimen surface. The specimens polished with $0.05\mu m$ Al_2O_3, however, showed no pits at all. A smooth surface thus exhibits a high MIC resistance. The HAZ may also show a changed internal structure and composition and may in some circumstances act as a location where corrosion is easily and preferentially initiated, the phenomenon concerned long being known as weld decay. Important research tasks in future thus concern the relationship between these changed characteristics and micro-organisms as well as whether or not it is appropriate to perform some form of post-weld heat treatment to prevent MIC.

3. Mechanism of MIC and micro-organisms involved

The possibility that micro-organisms may be implicated in corrosion was first mooted around 100 years ago when the key aspects of the corrosion mechanism responsible for "microbiologically influenced corrosion" and the characteristics of the micro-organisms involved were examined. In the 1930s,strenuous research efforts were launched from the perspective that micro-organisms have a role to play in corrosion. The 1980s saw the advent of quantitative investigations. Various theories have been postulated about the corrosion mechanism. Ito[8] sees corrosion as being indirectly caused by the metabolism of micro-organisms, Shimodaira[9] reports the corrosion process of metals is promoted by the presence of micro-organisms. To summarize , available data suggest that (1) corrosion is due to acids being formed;(2) anodic and cathodic reactions are promoted by metabolites being formed;(3) electrons from the metal are consumed by the metabolic process of micro-organisms multiplying ; (4)oxygen or ion concentration cells are formed by concentrations of metabolic products;etc. West[10] states that micro-organisms produce corrosive chemical substances, such as e.g. protons and sulphide ions, or that they catalys electrochemical reactions. In an investigation using sea water, Amaya and Miyuki[11] report that hydrogen peroxide(H_2O_2) is formed by the metabolic reactions of adhering micro-organisms and that the stainless steel surface is thereby locally corroded.

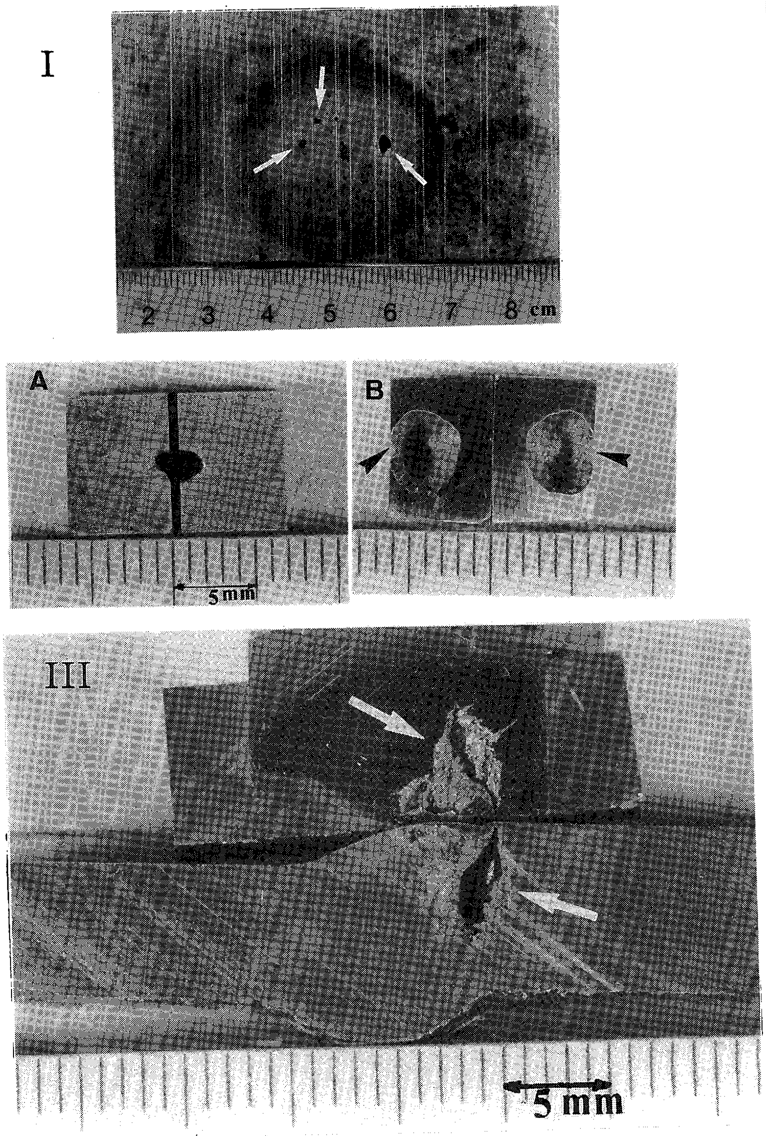
By-products of metabolism or chemical reactions are thus deeply involved at locations where micro-organisms reside. Electrochemical techniques are therefore used as research methods. More recently , attempt have also been made to analyses by-products of metabolism (sometimes typified by biofilms)using state-of-the art analytical techniques. The characteristics of micro-organisms are similarly an important topic, which should also be analyses by microbiological research techniques, such as simulations using cultured and isolated micro-organisms.

The questions has also been raised as to whether micro-organisms might not corrode metals directly . Some species of micro-organism are known to be sensitive to magnetism and are stated to be able to synthesize magnetite(Fe_3O_4) by internal absorption of Fe[12]. If this reaction could be established in the MIC process, it could well be manifested as direct corrosion of metals. It is also noted that the more liquid entrained by a metal, the higher the activity of the micro-organisms corroding it, and that metals have a profoundly sterilizing effect on micro-organisms. It is therefore necessary to separate micro-organisms from lumps of rust and metabolic products and to determine the components by analysis of the metal elements contained in them. More accurate analytical techniques are expected to emerge.

These micro-organisms are reported to be able to thrive at pH values of 0-11, temperatures of 273-353K, and pressures of 100MPa and are found in petroleum products, soil, and oozes on the beds of rivers, lakes, and seas. Some typical micro-organisms are described below.

3.1 Iron bacteria

Iron bacteria[8,9] have an ability to consume the dissolved oxygen in liquids and to turn Fe^{2+} into insoluble Fe^{3+} . Many species are known to exist and



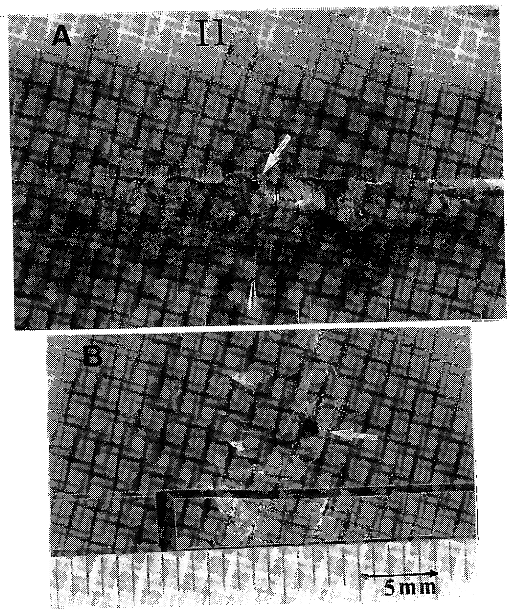


Fig. 3 Corrosion of 304 stainless steel pipe.
(I)pits shown surface of base metal. (A) and (B) shows cross section
(II)weld metal surface (arrow)
(III)cross section of weld metal

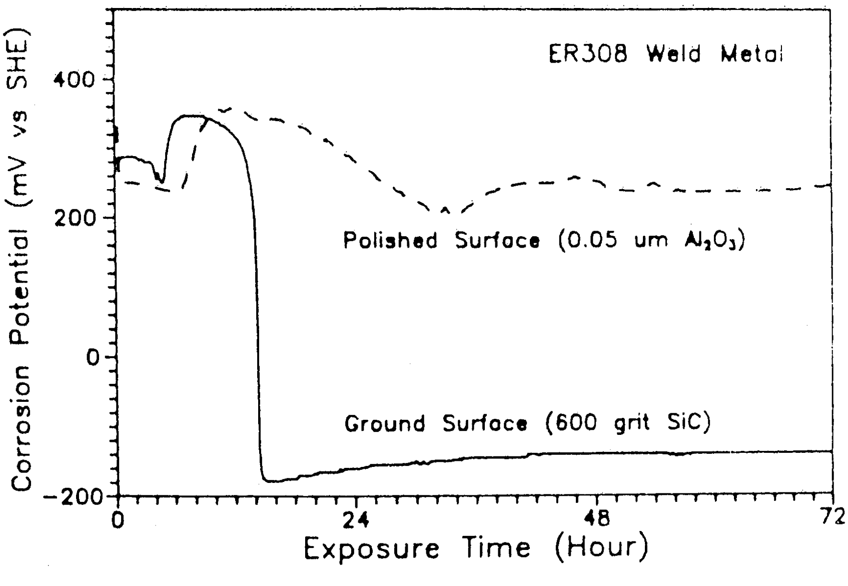


Fig. 4 Surface finish of 308 weld metal and MIC initation susceptibility

thrive in ground water and soil. They are responsible for lumps of rust being formed inside water pipes. This is due to Fe_3O_4FeOOH being precipitated by the oxidation of $Fe(OH)_2$. The oxygen deficient environment inside these lumps of rust leads to the formation of oxygen concentration cells, which accelerate corrosion. The interior additionally provides a favorable environment for anaerobic bacteria to thrive. These prefer environment conditions of pH=6-8 and a temperature near 297K, and multiply more readily where more iron and organic matter are present.

3.2 Sulphur-oxidizing bacteria

Sulphur -oxidizing bacteria[8,9] are aerobic and thrive in soil, oil fields and ooze. They produce suphuric acid by oxidation of incomplete sulphur oxides, thereby increasing the oxidisability of the environment.

They interact with other bacteria to form slimes and adhere to metal surfaces to form oxygen concentration cells. Their preferred conditions are pH=2-4 and a water temperature of around 303K.

3.3 Iron-oxidizing bacteria

Iron-oxidizing bacteria are a species of sulphuric - oxidizing bacteria described above. They have an ability to make Fe^{3+} by oxidation of Fe^{2+} and thrive especially well in acid solutions. They are aerobic and prefer environmental conditions with a pH<3. They are used in bacteria leaching and the treatment of effluent discharged from sulphur mines[12].

3.4 Hydrogen bacteria

Hydrogen bacteria[13] are implicated in corrosion in aerobic environments. They thrive in tap water and activate molecular hydrogen.

3.5 Sulphate-reducing bacteria

Sulphate-reducing bacteria[8,9] are anaerobic and thrive in soil, and the oozes of paddy fields, lakes, rivers , and seabeds. They reduce SO_4^{-2} to S^{-2} via $S_2O_3^{-2}$ and corrode ferrous materials by forming H_2S. Their preferred conditions are pH=7 and a temperature near 303K.

3.6 Nitrate-reducing bacteria

Nitrate-reducing bacteria[8-9] are anaerobic and initiate corrosion by forming ammonia through reduction of nitrates. They thrive in soil, peat and polluted rivers and prefer environments with pH=7-9 and a near-ambient temperature. Also known to exist are nitration bacteria which produce nitrous and nitric acids by oxidation of nitrogen compounds.

3.7 Aluminum(alloy)-corroding bacteria

There have been reports of accidents being caused by partial structural corrosion of the Al alloy fuel tanks of aircraft and associated fuel leakage. Inoue[14] reports that cladosporium leginae(a species of mould) and micrococcal bacteria that thrive in jet aviation fuels corrode Al alloys[15].

This caseis also explained as being due to the fact that micro-organisms produce organic acids, though there is also the suggestion of its being due to the essential biochemical activity of micro-organisms. This aspect, however, continues to remain rather obscure.

The foregoing account has basically described the nature of micro-organisms relate to MIC. MIC normally appears to stem from the combined activity and involvement of a multiplicity of micro-organisms. It is therefore in many cases difficult to run laboratory - scale tests to simulate the environmental field conditions in which corrosion is initiated.

Reference 16 describes some results obtained during the first stage of laboratory-scale simulations using various types of stainless steel weld and the residual liquid obtainable from MIC-affected effluent treatment plants.

The liquid used was basically neutral and contained a high concentration of Cl^-· Culturing of the micro-organisms residing in the liquid revealed some 6-7 different species of micro-organism. **Figure 5** gives a typical example . These bacteria are now at the specification stage. Various types of stainless steel weld were immersed in the liquid and kept in an incubactor at a constant temperature of $40^{\circ}C$. The lumps of rust formed on the specimen surfaces were examined.

Figure 6 shows the corrosion pits found on 316L weld metal after 62 days. Both preferentially corroded zones and skeletal residual zones can be clearly seen. The skeletal zones are shown to be Cr-rich when analysed by EDX. These zones are estimated to be delta ferrite. The process though to be taking place here is that the base austenite structure is preferentially attacked, leaving the skeletal residue. As corrosion progresses, however, these zones also corrode and perforate. **Figure 7** shows the micro-organisms found in and near the corrosion pits. The specimens used were

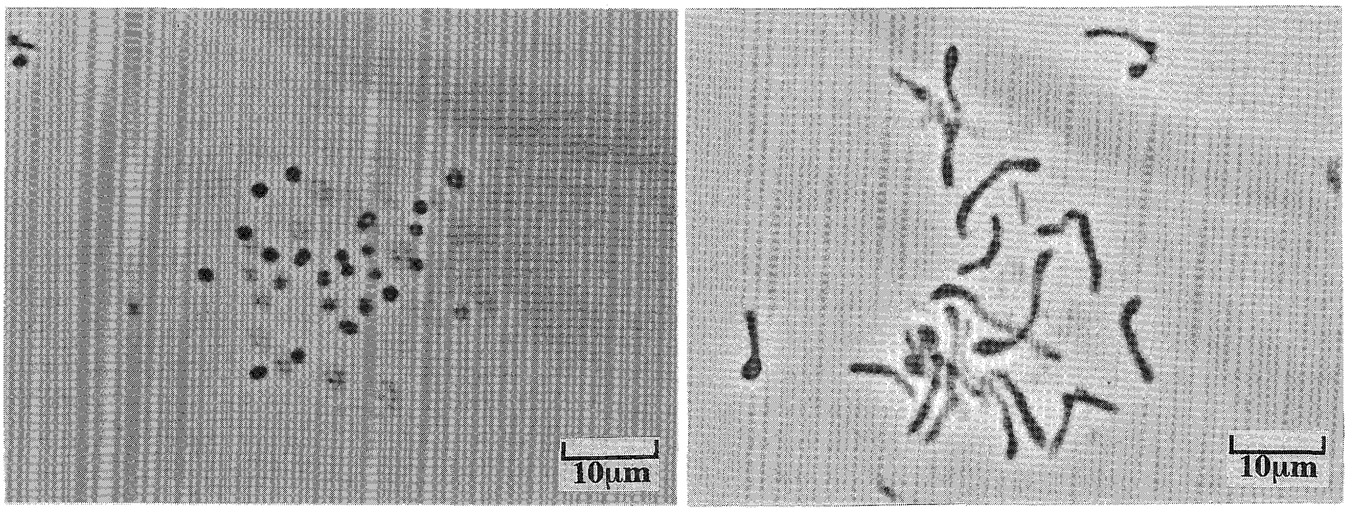


Fig. 5 Example of micro-organisms culutured in test liquid

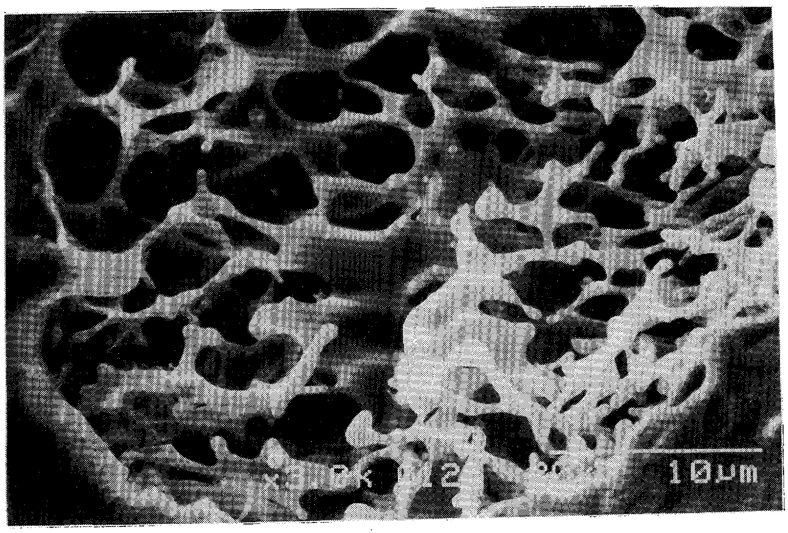


Fig. 6 Corrosion of 316L weld metal. The γ is preferentially attacked , leaving the delta ferrite

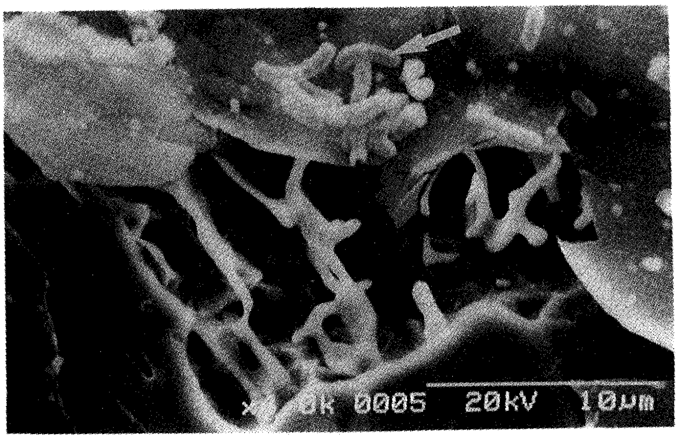


Fig. 7 Micro-organisma in and near corrosion pit in 308 weld metal(arrow)

similar to the MIC-free 308 stainless steel weld metal specimens used in 62 day immersion tests, being tested here in long-term simulations lasting 240 days. After the required test time had elapsed, the specimens were removed, and the micro-organisms subjected to a fixing treatment and examined by SEM. As indicated by the arrow, the micrograph included shows colonies of jellybean -like bacilli of several μm size near the corrosion pits. These bacteria are present in large numbers, forming colonies in the corrosion pits and appear to be implicated in corrosion. However, when , the same liquid was sterilized in an autoclave and the same tests were run, no corrosion was found.

The foregoing refers to an example of micro-organisms affecting metals. Concrete and stone structures, however, are also susceptible to severe damage caused by MIC. Reference 17 reports that the concrete structures of culverts and water purification plants are attacked by sulphur-oxidizing bacteria, and Ref.18 reports that printed circuit substrates and GaAs sintegrated circuit substrates are damaged by moulds.

Methods of preventing MIC are briefly outlined below. Although monitoring techniques continue to be developed, no effective treatments appear to be available at present. Replacement and repair of corroded parts are obvious expedients It is also possible to apply treatments with sterilizing chemicals (bromine compounds, hydrogen peroxide, etc.) These substances, however, cause environmental pollution, and new, environmentally friendly countermeasures should be sought.

4. Conclusions

The first symposium on MIC held in Tokyo provided an occasion for the MIC situation in Japan to be reported (organized by the Japanese Corrosion Protection Association in September 1994). It would appear that Japan lags behind Europe and America in launching research, with especially little research being mounted in welding related fields. MIC is closed related to a number of research fields and calls for a number of scientific disciplines to be brought to bear upon it, such as microbiology , materials science, corrosion technology, welding and joining technology, etc. It therefore appears necessary to pursue research as an interdisciplinary effort between technologists and researchers in each of these fields. Research results would lead to the development of optimum joining technologies, preventive measures, and materials with good MIC resistance and would also be a groundbreaking step in the application of micro-organisms for welding and joining processing surface refinement, etc.

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