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(54) Method of preventing stress corrosion cracking in machines or machine parts made of austenitic cast iron.

(57) Austenitic cast iron has excellent corrosion resisting properties and has been preferentially used in machines or machine parts intended for handling corrosive fluids such as seawater. Cases, however, have been reported of machines or machine parts made of austenitic cast iron failing after they had been put to prolonged service at relatively low temperatures. The present inventors have located stress corrosion cracking as the cause of this failure. The present invention therefore provides a method of preventing the occurrence of such stress corrosion cracking in machines or machine parts made of austenitic cast iron by subjecting them to cathodic polarization, such cathodic polarization preferably being such that the applied potential is at least 50 mV more base (less noble) than the stabilized natural potential.

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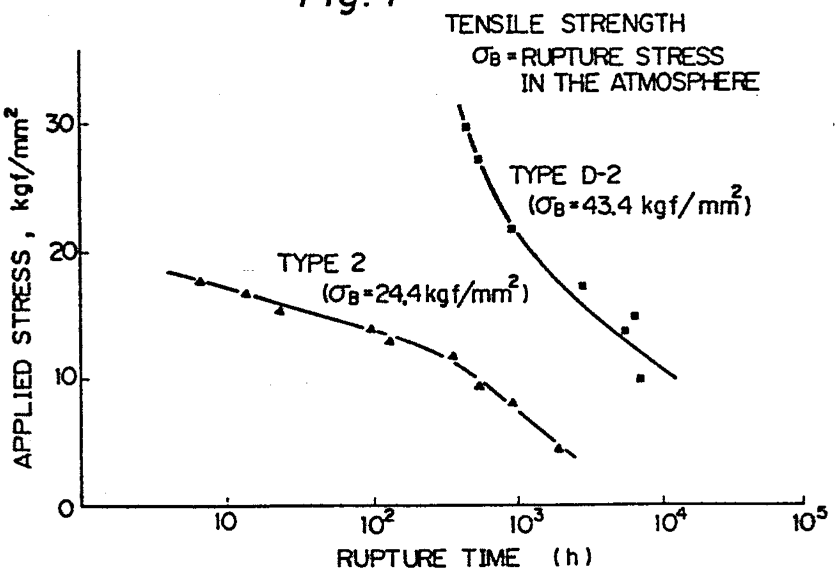
Fig. 1


TENSILE STRENGTH
σ_B = RUPTURE STRESS IN THE ATMOSPHERE
TYPE D-2
(σ_B = 43.4 kgf/mm^2)
TYPE 2
(σ_B = 24.4 kgf/mm^2)
APPLIED STRESS, kgf/mm^2
0
10
20
30
10
10^2
10^3
10^4
10^5
RUPTURE TIME (h)

METHOD OF PREVENTING STRESS CORROSION CRACKING IN MACHINES OR MACHINE PARTS MADE OF AUSTENITIC CAST IRON

The present invention relates to a method of preventing the occurrence of stress corrosion cracking in machine or machine parts made of austenitic cast iron.

Austenitic cast iron, i.e., ASTM A 436 of the flaky graphite type or ASTM A 439 of the nodular graphite type, containing 13.5 - 22 wt% of Ni (all percents noted hereinafter are by weight) exhibits good corrosion resistance in seawater and other corrosive environments containing chloride ions (Cl^-) and is preferentially used in pumps, valves and piping associated with the handling of concentrated or unconcentrated seawater.

The resistance of austenitic cast iron to general corrosion is such that the corrosion rate is only about 0.1 mm/year in seawater at ordinary temperatures. Unlike mild steels and cast iron, the increase in the rate of general corrosion in austenitic cast iron situated in flowing seawater over that in standing seawater is negligible, and if the seawater flows faster, the rate of corrosion is even seen to decrease. Additionally, austenitic cast iron is not susceptible to localized corrosions such as the crevice corrosion and pitting corrosion that are common to stainless steel. Because of the balanced resistance to various forms of corrosion, austenitic cast iron is extensively used in machines and machine parts that handle seawater and other corrosive fluids.

Cases, however, have been reported of machines or machine parts made of austenitic cast iron handling seawater or enriched seawater devleoping cracks a considerable time after the start of service. One case of such an accident occurred in pumps made of austenitic cast iron (ASTM A 436, Type 2) that were handling enriched seawater (7% NaCl) at ca. 33°C. The present inventors made extensive studies on the accident in different aspects including the possibility of defects in the pump material, its strength, stress during operation and fatigue, but no exact cause of the accident could be identified.

The studies mentioned above did not cover stress corrosion cracking (hereunder abbreviated to SCC) as a possible factor responsible for the failure of the pumps under relatively low stress. There are not reported cases of SCC occurring in austenitic cast iron used in salt water in the vicinity of ordinary temperatures. The occurrence of SCC in boiling-42% $MgCl_2$, boiling-20% NaCl and NaOH at 90% of the yield stress has been reported in Engineering Properties and Applications of the Ni-Resists and Ductile Ni-Resists (INCO). The general understanding has been that austenitic cast iron has high SCC resistance in a chloride environment. Alloys having the austenitic structure such as Cr-Ni austenitic stainless steel are well known to be susceptible to SCC in chloride solutions, but very few cases have been reported on the occurrence of SCC at temperatures lower than 50°C. SCC may occur at ordinary temperatures as a result of hydrogen embrittlement, but the susceptibility of the austenitic structure to hydrogen embrittlement is low.

The present inventors made various studies to unravel the behavior of austenitic cast iron in relation to its failure in seawater and other corrosive environments. As a results, the inventors have located the cause of such failure and devised a method for its prevention.

The present invention, therefore, provides a method for preventing the occurrence of SCC in machines or machine parts made of austenitic cast iron which are intended for handling salt water, or any type of the solutions that contain chloride ions Cl^- such as seawater, enriched seawater and diluted seawater. This method is characterized by cathodic polarization of the machine or machine part of interest.

Fig. 1 shows applied stress vs. rupture time characteristic curves for austenitic cast iron species, Type 2 and Type D-2, submerged in 7% NaCl solution at 33°C;

Fig. 2 shows applied potential vs. rupture time characteristic curves for the same austenitic cast iron species;

Fig. 3 shows a flow rate vs. natural potential curve for Type D-2 cast iron submerged in 3% NaCl solution at 25°C;

Fig. 4 shows applied potential vs. rupture time characteristic curves for Type D-2 cast iron in flowing NaCl solution;

Fig. 5 is a sketch of two anode metal pieces attached to a test piece having a tapered diameter of 3 mm in the middle portion; and

Fig. 6 is a sketch of the same test piece having a coat of paint which comprises an anode metal powder dispersed in a resin.

In order to check for the possibility of the occurrence of SCC in austenitic cast iron, the present inventors made the following SCC test. The chemical composition of each of the test specimens and their tensible strengthes (rupture stresses in the atmosphere) are shown in Table 1. The same test was conducted on four samples of ferritic cast iron and one sample of austenitic stainless steel.

All samples of the austenitic cast iron had been annealed (heating at 635°C for 5 hours followed by furnace cooling) in order to relieve any residual stress. The constant load tension test was conducted by applying varying stresses to a test piece (5 mm^{ϕ}) submerged in 7% NaCl at 33°C. The two samples of Type 2 and Type D-2 were also tested in 3% NaCl, 1% NaCl and natural seawater at 25°C by applying 80% of the tensile strength of the respective samples. The results are shown in Table 2.

Table 1 SCC Test Materials

Materials		Chemical composition wt%									Tensile strength kgf/mm^2
		C	Si	Mn	P	S	Cr	Ni	Cu	Mo	
Austenitic cast iron	ASTM A436 Type 1	2.50	1.58	1.65	-	0.018	2.13	15.47	5.93	-	24.2
	" Type 2	2.66	2.67	0.78	-	0.010	2.38	18.90	-	-	24.4
	ASTM A439 Type D-2	2.59	2.52	0.85	0.009	-	2.20	19.00	-	-	43.4
	" Type D-3	2.45	2.79	0.91	0.025	-	2.55	29.46	-	-	42.5
	" Type D-4	2.40	5.58	0.88	0.024	-	4.58	29.90	-	-	42.2
	ISO draft proposal S-NiMn 137	2.74	2.81	6.69	0.026	-	0.15	13.57	-	-	42.9
Ferritic cast iron	JIS FC20	3.53	2.23	0.41	0.062	0.141	-		-	-	29.9
	" FCD45	3.26	2.49	0.76	0.047	0.013	-		-	-	48.8
	ES51F	3.09	2.76	0.48	0.054	0.067	1.17	0.13	-	-	27.2
	ES51	3.14	3.77	0.67	0.064	0.026	1.14	0.09	-	-	61.2
Austenitic stainless steel	JIS SCS 14	0.06	1.08	1.13	0.021	0.018	19.10	10.84	-	2.21	48.2

Table 2 SCC Test Results (Mean of two runs)

Materials		Rupture time (h)			
		33°C, 7% NaCl	25°C, 3% NaCl	25°C, 1% NaCl	25°C, natural seawater
Austenitic cast iron	ASTM A436 Type 1	2.8	-	-	-
	" Type 2	3.5	4.5	5.2	4.3
	ASTM A439 Type D-2	135	201	251	187
	" Type D-3	660	-	-	-
	" Type D-4	520	-	-	-
	ISO draft proposal S-NiMn 137	73	-	-	-
Ferritic cast iron	JIS FC20	no crack at 2000 hrs	-	-	-
	" FCD45		-	-	-
	ES51F		-	-	-
	ES51		-	-	-
Austenitic stainless steel	JIS SCS 14		-	-	-

As one can see from Table 2, all samples of the austenitic cast iron failed in the test period although the applied stress was such that the samples would not fail in the atmosphere. This was obviously the result of the SCC that was caused by the interaction of the corrosive attack of the aqueous NaCl solutions and the applied stress. Type 2 and Type D-2 also developed SCC in the 3% NaCl, 1% NaCl and natural seawater at 25°C. From these results, one can readily see that SCC would occur in austenitic case iron whether it is submerged in concentrated or diluted seawater. The ferritic cast iron species, JIS FC20, JIS FCD45, ES51F and ES51, as well as the austenitic stainless steel JIS SCS 14 did not fail in a 2,000-hour period and not a single tiny crack developed in the test pieces.

The above observation that austenitic cast iron develops SCC in salt water in the vicinity of ordinary temperatures whereas ferritic cast iron and austenitic stainless steel are free from such phenomenon was first discovered by the present inventors. It was quite surprising and in conflict with metallurgical common sense to find that SCC should occur in austenitic cast iron submerged in salt water at ordinary temperatures or in its vicinity.

In order to further study the behavior of SCC in austenitic cast iron, samples of Type 2 and Type D-2 were checked for the relationship between applied stress and rupture time using test pieces with a diameter of 12.5 mm. This diameter was greater than that of the samples used in the test conducted to obtain the data shown in Tables 1 and 2. The reason for selecting such increased diameter was that it was necessary to obtain data that would be applicable to large-size equipment such as large pumps in consideration of the "size effect", i.e., the fact that larger diameters prolong the rupture time. The test was conducted in 7% NaCl at 33°C, and the test method was the same as used for obtaining the data shown in Tables 1 and 2.

The test results are shown in Fig. 1, from which one can see that both Type 2 and Type D-2 failed in shorter periods under increasing stresses. Type 2 failed at 2,000 hours under a stress of 5 kgf/mm^2 which was only 20% of its tensile strength whereas Type D-2 failed at 7,000 hours under a stress of 10 kgf/mm^2 which was 23% of its tensile strength. Surprisingly enough, SCC occurred in austenitic cast iron even under very low stressed, suggesting the possibility that machines or machine parts made of austenitic cast iron would fail during service in salt water.

Several methods are available for preventing the SCC-induced failure of machines or machine parts made of austenitic cast iron. One is to make a machine or machine part having the lowest possible design stress, but this is not economically feasible since such a machine or machine part either has reduced capabilities or requires an increased wall thickness. Another method is to insulate the machine or machine part from the corrosive environment by providing a lining. However, not only does the lining add to the cost of the machine or machine part but also a highly reliable lining is difficult to obtain. The great problem associated with the use of the lining is that the unique corrosion resisting properties of austenitic cast iron are not utilized to the fullest extent, and lower grade materials such as common cast iron may be used as the substrate if they are lined. A third way is to use an austenitic cast iron having a higher Ni content because the data in Table 2 shows that such cast iron had longer rupture periods. However, even such high Ni austenitic cast iron is susceptible to SCC, and additionally, the inclusion of much Ni increases the cost.

Therefore, the best way is to directly prevent the occurrence of SCC in austenitic cast iron; if this is possible, the machines or machine parts made of austenitic cast iron can be used in salt water without experiencing SCC-induced failure, and furthermore, economical machine design can be realized since the possibility of a drop in rupture stress within corrosive environments is eliminated.

The mechanism behind SCC in austenitic cast iron must first be unravelled in order to devise a method for its prevention. Two types of SCC are generally known: an example of the first type of SCC is that which occurs in austenitic stainless steel under a chloride environment, and in this type of SCC, the anodic reaction causes progressive cracking; an example of the second type of SCC is that which occurs in high-strength steels in an environment containing hydrogen sulfide, and in this type of SCC, atomic hydrogen formed by cathodic reaction enters the structure to cause its embrittlement. In a special case, the two types of SCC combine to accelerate cracking. With a view to unravelling the mechanism behind SCC in austenitic cast iron, the present inventors conducted the following test.

Two sets of Type 2 and Type D-2 samples were provided; one set of samples was subjected to an SCC test while they were held at varying applied potentials, and the other set was tested under their natural potentials. The test pieces had a diameter of 3 mm. Type 2 samples were subjected to a stress of 15 kgf/mm^2 and Type D-2 samples were subjected to a stress of 34.7 kgf/mm^2. The samples were submerged in 7% NaCl at 33°C. The rupture times as a function of applied potential vs. SCE (saturated calomel electrode) were measured and are shown in Fig. 2. In the test conducted under the natural potentials of the samples, Type 2 failed at 4 hours, with the natural potential varying from -430 mV to -490 mV. Type D-2 failed at 23 hours, with the natural potential varying from -460 mV to -550 mV. The rupture times of both Type 2 and Type D-2 were appreciably reduced when they were held at potentials more noble than the natural potentials. On the other hand, the rupture times were considerably prolonged by setting the samples at potentials more base (less noble) than the natural potentials. At -570 mV, neither Type 2 nor Type D-2 cracked even after 350 hours. At more base -800 mV, no crack occurred in either type of samples after 420 hours. These data show that the SCC in austenitic cast iron is of the anodic dissolution type (Active Path Corrosion Cracking - APC-Type) which is accelerated by anodic polarization and inhibited by cathodic polarization.

In order to further delve into the conditions for providing the cathodic polarization that is necessary to prevent the occurrence of SCC in austenitic cast iron, the present inventors investigated the behavior of SCC in Type D-2 samples submerged in flowing 3% NaCl at 25°C. Fig. 3 shows the relationship between the flow rate of the NaCl solution and the natural potential at 48 hours. As one can see from the figure, the natural potential was initially -530 mV when the NaCl solution was not flowing, but the potential rapidly became noble as the flow rate increased, and at flow rates of 0.5 m/sec and higher, the potential remained substantially constant at about -440 mV. The present inventors therefore conducted another experiment, with the flow rate of 5 m/sec selected as a typical value simulating the flowing state of the NaCl solution. Fig. 4 shows the applied potential vs. rupture time for Type D-2 under an applied stress of 34.7 kgf/mm^2. As one can see from Fig. 4, when no control was effected over the potential, Type D-2 failed at 28 hours, with its natural potential varying from -410 mV to -435 mV. When Type D-2 was held more base than the natural potential, the rupture time was extended and no crack occurred at -490 mV even after 1,200 hours. In other words, the natural potential of Type D-2 submerged in a flowing NaCl solution became more noble than when the solution was standing, but at the same time, the applied potential necessary for preventing the occurrence of SCC also became more noble. These observations are associated with the behavior of SCC in NaCl solutions but it will be radially understood that the same applies to seawater.

The present invention is based on the above findings and is characterized by preventing the occurrence of SCC in austenitic cast iron by means of cathodic polarization. The applied potential necessary for preventing the occurrence of SCC is preferably more base than about -570 mV in the case of a standing salt water in the vicinity of ordinary temperatures, and is preferably more base than about -490 mV if the salt water is flowing. However, even if these potentials are not reached, the life of austenitic cast iron can be significantly extended by means of cathodic polarization.

The natural potential of austenitic cast iron will vary depending upon the concentration of salt water, its temperature, flow rate and the immersion time. In the experiment conducted by the present inventors, the natural potentials of the samples of austenitic cast iron were not sufficiently stabilized for examining the effects of applied potential on SCC. Therefore, another experiment was conducted to measure the natural potentials at 48 hours which was considered sufficiently long for their stabilization. The results are shown in Table 3, which also lists the applied potentials necessary for preventing the occurrence of SCC in austenitic cast iron.

Table 3

Sample	Test conditions			Natural potential vs. SCE mV	Crack-resistant potential vs. SCE mV
	NaCl conc. wt%	Temperature °C	Flow rate m/sec		
Type D-2	3	25	5	-440	-490
Type D-2	7	33	0	-550	-570
Type 2	7	33	0	-520	-570

The above data show that although the natural potentials, and hence, the conditions for cathodic polarization necessary for preventing the occurrence of SCC, vary depending upon the specific environment, the development of SCC can be prevented almost completely by performing cathodic polarization to such an extent that the applied potential is at least 50 mV more base than the stabilized natural potential for the environment concerned. Even if the differential potential is less than 50 mV, the life of austenitic cast iron can be significantly extended by means of cathodic polarization.

Cathodic polarization can be realized either by the impressed current method (forced drainage method) using a rectifier, battery or a dc generator, or by the galvanic anode method using the potential difference between dissimilar metals. The former method has the advantage that a desired potential can be selected. The anode for the galvanic anode method may be made of any of the metallic materials that are more base than austenitic cast iron, for example, iron, ferritic cast iron, zinc, aluminum, magnesium, and paint compositions having these metals dispersed in resins. These materials may be used either alone or in combination.

Example

The effects of cathodic polarization on SCC using the impressed current method are clear from the data shown above. Therefore, in this example, the effects of cathodic polarization by the galvanic anode method were investigated. Each of the test pieces (Type D-2) used had a middle portion with a diameter of 3 mm, as shown at 1 in Fig. 5 or 6. They were submerged in 7% NaCl at 33°C and placed under an applied stress of 30 kgf/mm^2.

Fig. 5 illustrates a test piece to which anode metal pieces 2 (30 x 30 x 10 mm) were attached. Fig. 6 shows a test piece provided with an anodic coat 3 formed from a paint composition having a powder of anodic metal dispersed in a resin.

In the test, the following six anode metals were used: ferritic cast iron JIS FC20, mild steel JIS SS 41, pure iron, aluminum, zinc and magnesium. The following two paint compositions were used: zinc paint and aluminum paint. The zinc paint contained 36 vol% of zinc in an epoxy resin whereas the aluminum paint contained 45 vol% of aluminum in an epoxy resin. The test results are shown in Table 4.

Table 4 Protective Effects of Cathodic Polarization against SCC in Austenitic Cast Iron

Anode materials		Potential of the specimens vs. SCE mV	Results
No cathodic polarization		-520	failed at 25 hours
Anode metals	ferritic cast iron JIS FC20	-710	did not fail even after 500 hours
	mild steel JIS SS 41	-720	
	pure iron	-720	
	aluminum	-1100	
	zinc	-1100	
	magnesium	-1600	
Al paint		-950	
Zn paint		-900	

According to Table 4, the samples that were not subjected to cathodic polarization failed at 25 hours but those samples protected by cathodic polarization in accordance with the present invention did not fail even after 500 hours. These results were obtianed in 7% NaCl at 33°C and it will be readily understood that similar results can be obtained in seawater. Powders of anodic metallic material may be dispersed not in resins but in sodium silicate, and similar results are obtainable with such inorganic paints.

Claims:

1. A method of preventing the occurrence of stress corrosion cracking in a machine or machine part made of austenitic cast iron designed for handling salt water, said method being characterized by subjecting said machine or machine part to cathodic polarization.

2. A method according to Claim 1 wherein said machine or machine part made of austenitic cast iron is designed for handling salt water at ordinary temperatures or thereabout.

3. A method according to Claim 1 or 2 wherein said machine or machine part made of austenitic cast iron is a pump, valve or pipe.

4. A method according to any one of the preceding claims wherein said cathodic polarization is such that the applied potential of said machine or machine part is at least 50 mV more base (less nobel) than its natural potential.

Fig. I

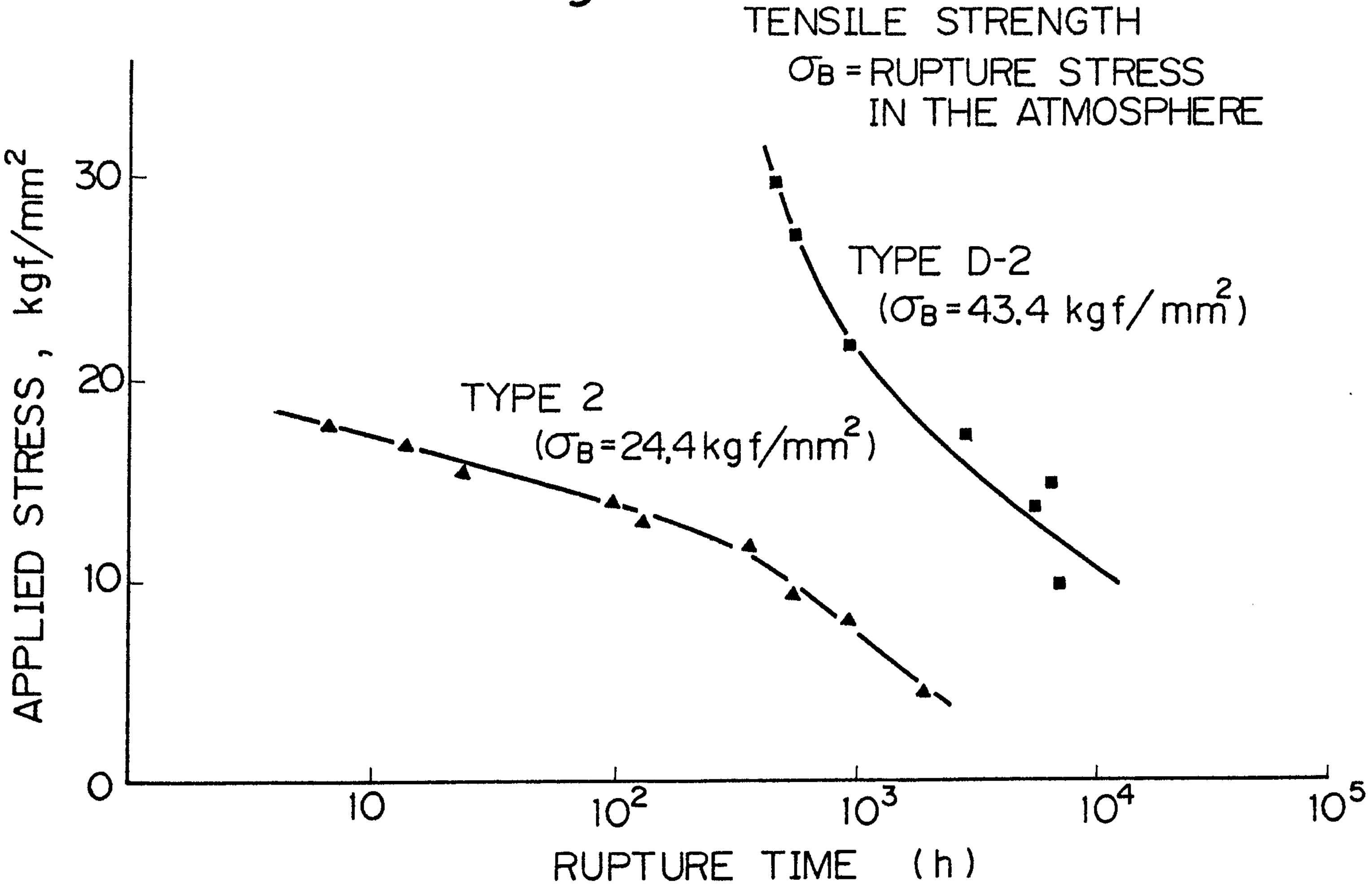
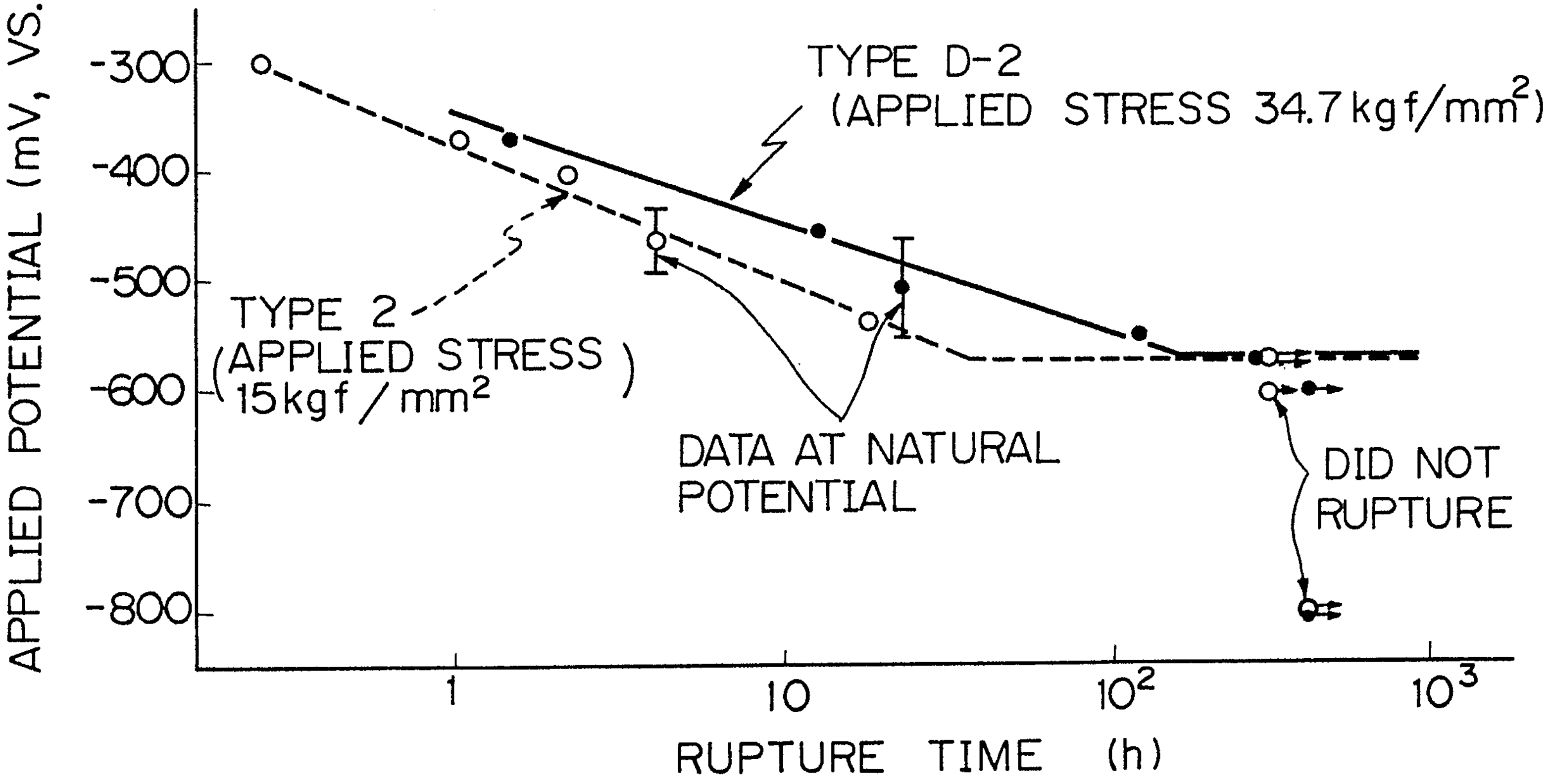

TENSILE STRENGTH
σ_B = RUPTURE STRESS IN THE ATMOSPHERE
TYPE D-2
(σ_B=43.4 kgf/mm^2)
TYPE 2
(σ_B=24.4 kgf/mm^2)
APPLIED STRESS , kgf/mm^2
0
10
20
30
10
10^2
10^3
10^4
10^5
RUPTURE TIME (h)

Fig. 2


APPLIED POTENTIAL (mV, VS. S.E.C.)
-300
-400
-500
-600
-700
-800
1
10
10^2
10^3
RUPTURE TIME (h)
TYPE D-2
(APPLIED STRESS 34.7 kgf/mm^2)
TYPE 2
(APPLIED STRESS 15 kgf / mm^2)
DATA AT NATURAL POTENTIAL
DID NOT RUPTURE

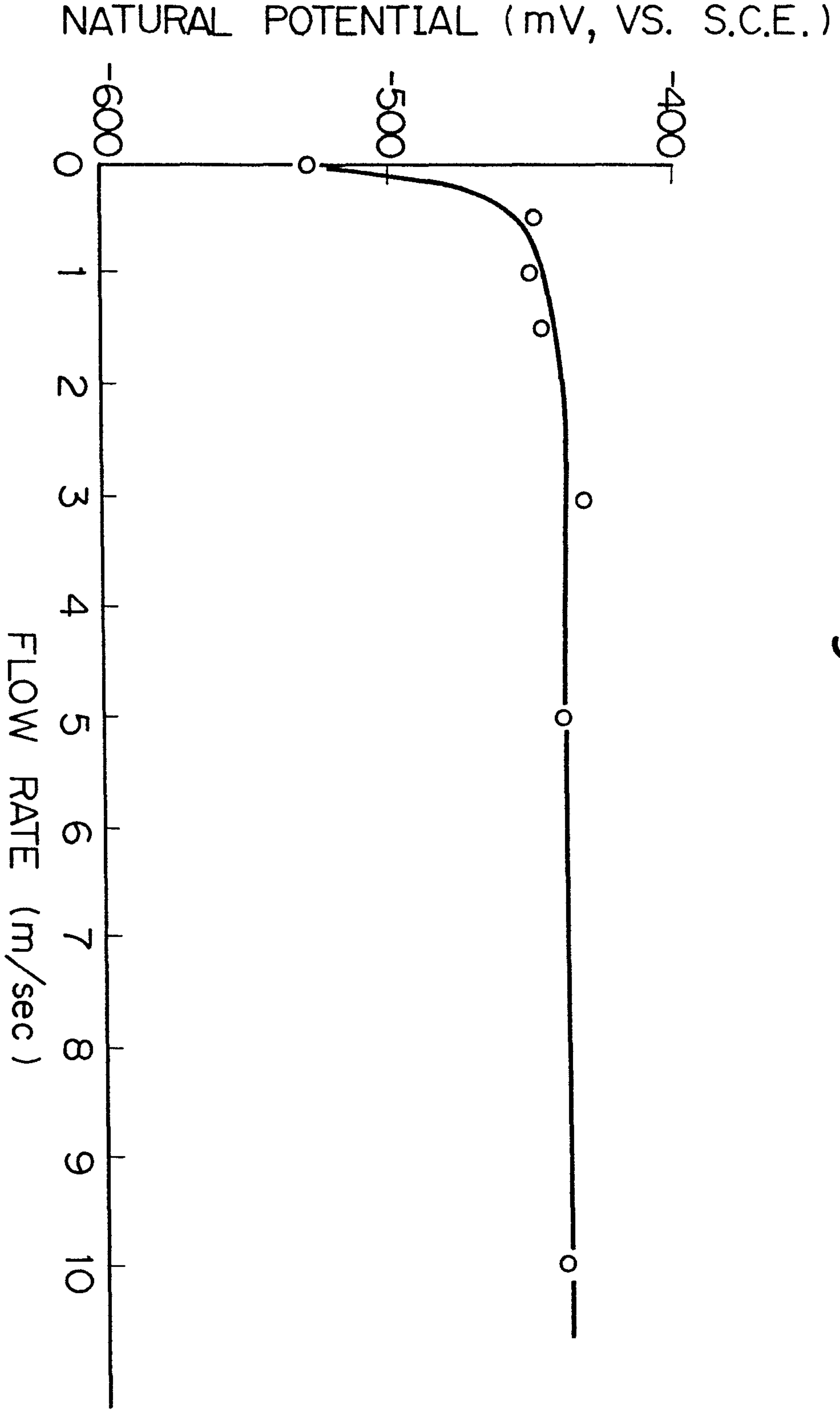

NATURAL POTENTIAL (mV, VS. S.C.E.)
-600
-500
-400
0
1
2
3
4
5
6
7
8
9
10
FLOW RATE (m/sec)

Fig. 3

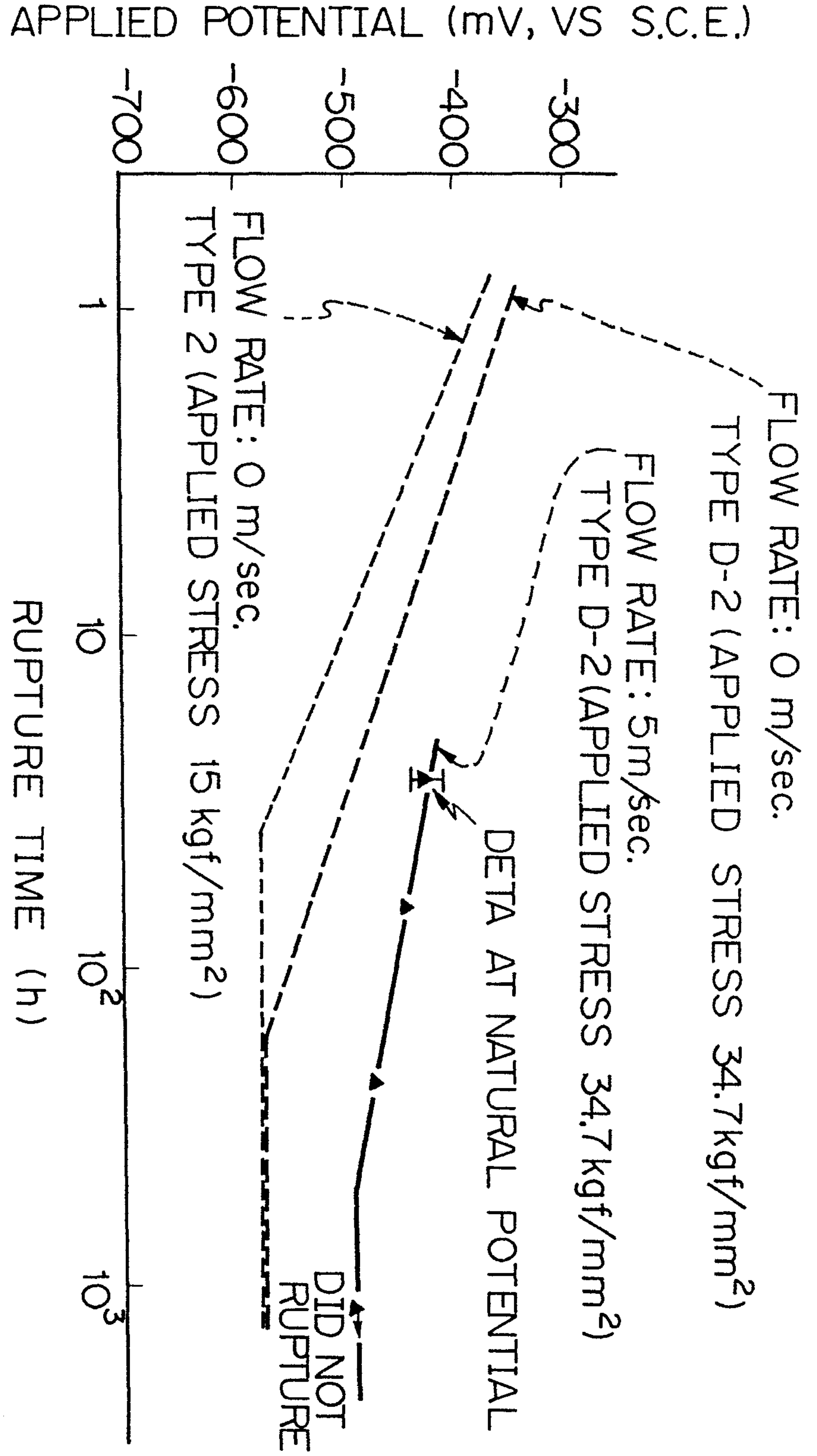


Fig. 4

APPLIED POTENTIAL (mV, VS S.C.E.)
-300
-400
-500
-600
-700
1
10
10^2
10^3
RUPTURE TIME (h)
FLOW RATE: 0 m/sec.
TYPE D-2 (APPLIED STRESS 34.7kgf/mm²)
FLOW RATE: 5m/sec.
TYPE D-2 (APPLIED STRESS 34.7kgf/mm²)
DETA AT NATURAL POTENTIAL
FLOW RATE: 0 m/sec.
TYPE 2 (APPLIED STRESS 15 kgf/mm²)
DID NOT RUPTURE

Fig. 5

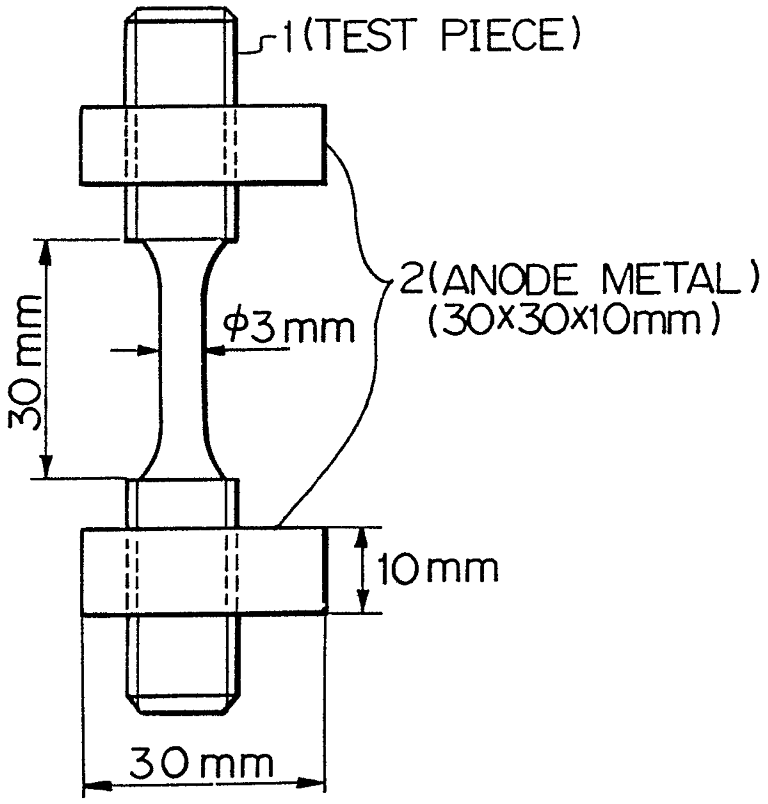
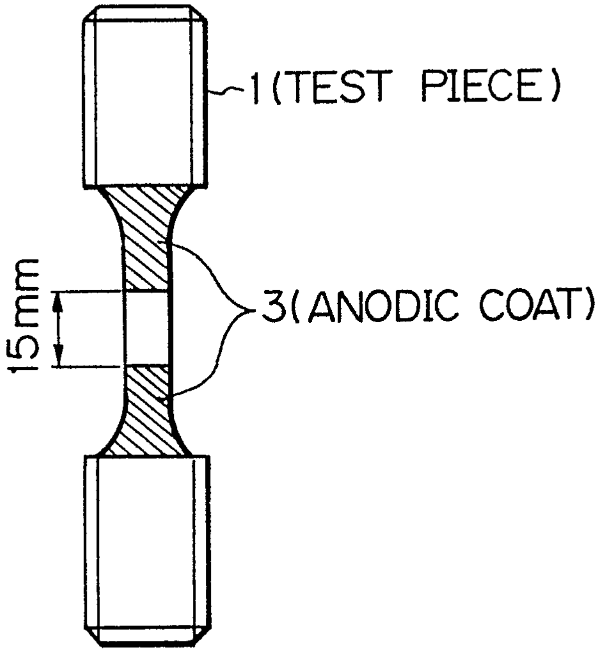

1(TEST PIECE)
2(ANODE METAL)
(30x30x10mm)
30mm
φ3mm
10mm
30mm

Fig. 6


1(TEST PIECE)
15mm
3(ANODIC COAT)