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Corrosion of AISI 316 and AISI 304 Stainless Steel with Iodine Vapour

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The weight loss of stainless steel in corrosion with iodine vapour has been studied in a temperature range of 500°~1000°C and a iodine vapour pressure range of 0.05 ~ 0.5 mmHg, using a thermobalance. In the initial stage of corrosion, the weight loss rate is largely influenced by solution treatment or surface treatment; the induction period, observed for solution-treated samples, is shortened or disappeared by fission-fragment irradiation, ion-bombardment or mechanical polishing, and in some cases corrosion is even accelerated by the surface treatments. A constant weight loss region follows the initial stage of corrosion. In this region, the weight loss rate is not dependent on treatment to the samples, and has a linear relationship with the vapour pressure of iodine. The rate is the largest at about 800°C and 750°C for AISI 316 s. s. and AISI 304 s. s. The rates in general are larger for AISI 304 s. s. than for AISI 316 s. s. below 700°C but almost the same above 800°C. Corrosion product layer is observed on the surface of the sample below 700°C. Based on these findings, the corrosion process is discussed. The deposition of corrosion product in a temperature gradient tube is also described

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1. Introduction

Research has been energetically carried out into the effects of the presence of stored nuclear fission products (FP) on the integrity of fuel cladding pipes accompanying the development of fast nuclear reactors characterized by the combustion of nuclear fuel to a high degree of combustion. Recently, the fission yield from FP has been high with regard to the integrity of stainless steel cladding pipes of mixed oxide fuels, and the participation of Cs or of Mo etc., with intense corrosivity, in the attack on the cladding pipes has been noted and often reported [1]. The fact that the participation of iodine in the FP in the attack on the cladding can become the cause of cladding rupture in the case of zircalloy has been clarified [2, 5, 4]. There have been many proposals regarding the possibility and course of participation of iodine in the attack on stainless steel cladding [5,6,7,8], but there have been few corroborative reports [9,10], and there are many unclear points. There are believed to be many problems in analysis of the [...]* system composed of fuel-FP-cladding, but to begin with iodine, there have been few reports in cases of high temperatures of the interaction between elemental iodine and stainless steel. There are many reports concerning the plate-out of iodine onto the surface of stainless steel pipes at comparatively low temperatures from the standpoint of determination of the behavior of iodine leaking into the cold pipes in the iodine and stainless steel system. These reports are believed to reflect the facts that the fission fragmentation rate of iodine in the FP is small in comparison to that of Cs etc., that the reaction of stainless steel and iodine is slow in comparison to that of zircalloy, and the fact that iodine is volatile, and poses major problems in the case of environmental contamination from leakage.

However, the temperature of use of the stainless steel cladding is often a high temperature near 700°C. At such high temperatures, the reaction with iodine due to the surface conditions of the cladding is believed to occur rapidly. Moreover, the possibility of stress corrosion cracking due to the presence of iodine is not entirely absent as in the case of stainless steel, even if the fission fragmentation rate of the iodine is small, as discovered in zircalloy cladding [2]. Conversely, there are also cases in which stainless steel is used at very high temperatures as cooling pipe material, as in the case of high temperature gas reactors. Consequently, the collection of information on the interaction at high temperatures between iodine and stainless steel is not only essential from the viewpoint of a necessary stage in the analysis of the interaction between actual fuel-FP-cladding, but is also essential from the

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viewpoint of estimating the transfer behavior and the chemical form of iodine at high temperatures, as well as from the viewpoint of estimating its effects on the integrity of the piping.

Nishio et al. [12] has also studied and reported the reaction between dilute iodine vapors in an argon gas flow and AISI 304 stainless steel as the material for pipes in high temperature gas reactors at high temperatures up to 700°C.

This report has studied the effects of solution treatment and of various surface treatments of stainless steel on the corrosion of AISI 316 and AISI 304 stainless steel due to iodine vapors in temperature ranges of 500°C to 1000°C, and iodine vapor pressure ranges of 0.05 to 0.5 mmHg, as a preliminary step in studying the interaction at high temperatures between iodine and stainless steel. The studies were conducted using thermobalances. The majority of corrosion products underwent partial volatilization at high temperatures, so that the amount of corrosion was measured as the weight loss of the stainless steel sample. The fission fragment irradiation damage and the heavy ion irradiation damage were studied by the irradiation [...]* method from the viewpoint of studying corrosion of stainless steel as cladding.

2. Experimental Method

2.1 Preparation of stainless steel samples

2.1.1 Configuration and Composition

The stainless steel samples were thin rectangular fragments 10 mm x 5 mm which were cut from thin plates approximately 0.25 mm thick of samples of AISI 316 and AISI 304 which were subjected to approximately 75% cold rolling. Holes approximately 2 mm in diameter were cut in them so that they could be suspended by quartz hooks of the thermobalance. They were also cleaned by [...]* in acetone for surface cleaning. The weight of one sample was approximately 90 mg. Table 1 illustrates the chemical composition of the samples.

2.1.2 Solution treatment and surface treatment

Some of the samples were subjected to solution treatment. Below, we will term the samples subjected to solution treatment as solution treated samples, while those without such treatment will be referred to as cold rolled samples. These were then subjected to surface treatment. The details of each treatment are given below.

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(1) Solution treatment. Samples were placed in transparent quartz tubes (inner diameter 6 mm ø) sealed at one end, and while exhaust was carried out from the other end (approximately -10^{-3} mmHg), the quartz tubes were placed in electric furnaces and were heated for one hour at 1050°C. At the end of heating, pure helium was introduced into the quartz tubes which were removed from the furnaces, and the quartz tubes were [...]*.

(2) Surface treatment.

a. Electro-polishing. A liquid containing small amounts of chromium trioxide was used in a compound solution of normal phosphoric acid (7 containers) and concentrated sulfuric acid (3 containers). The treatment was carried out for several minutes at a temperature of approximately 90°C and current density of 1 to 2 A/cm^2.

b. Passive state treatment. Following immersion for five minutes in 50 vol.% sulfuric acid at 70°C, the material is immersed for one hour in boiling 50 vol.% nitric acid.

c. Pickling. Immersion for 20 minutes in 20% nitric acid-2% fluoric acid at 60°C.

d. Mechanical polishing. Surface polishing using number 800 emery paper.

e. Fission fragment irradiation. The sample is sandwiched between natural [...]* thin metal plates and enclosed in aluminum foil and fixed. This is then vacuum sealed in a quartz ampul, and irradiated by JRR-2. The amount of irradiation involved that of one cycle of irradiation from the JRR-2VT opening and from two pneumatic tubes (5×10^{14}f.f./cm^2 and 1.5×10^{12}f.f./cm^2 in terms of fission fragment irradiation flux). Irradiation was followed by appropriate cooling, removal from the quartz ampul and experimentation.

f. Ion bombardment. 1.8 MeV Ar^{++} ions were irradiated on the surface of the sample in a vacuum (approximately 10^{-8} mmHg) using a 2 MeV Van de Graaff accelerator. Four amounts of irradiation were used: 7×10^{12}, 5×10^{16}, 8×10^{15} and 5×10^{16} Ar^{++}/cm^2.

2.2 Preparation of iodine crystals

The iodine crystals which are the raw material producing iodine vapor are commercial material (in contact with the atmosphere and believed to have adsorbed or incorporated air or water) which were distilled and refined by the method illustrated in figure 1. The distillation method is based on that indicated

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in literature [2]. The operations are discussed below. In figure 1, coarse iodine crystals are loaded, and then the loaded part is immersed in ice water, and air in the system is exhausted. At this time, the part from which refined iodine should be extracted was heated on a burner and gas was removed. Next, the precipitate was immersed in ice water, while the loaded portion was immersed in [...]* at 90 to 100°C and warmed, whereupon the iodine from the loaded portion was evaporated, while that in the extracted part was extracted. The saturated vapor pressure of iodine at -°C is 0.03 mmHg, and since the vapor pressure of water is 4.6 mmHg, a certain degree of water removal is possible through the aforementioned operations. In addition, the internal air could also be eliminated. The water or iodine which passed through the extracted part was collected by liquid nitrogen trap. In precipitation of iodine of appropriate [...]*, the inlet and outlet of the extraction part is [...]*, and is then set on the reaction equipment (thermobalance) described below.

2.3 Method of measuring corrosion rate

The majority of the corrosion product of stainless steel due to iodine vapors is evaporated from the surface of stainless steel at high temperatures. Consequently, the amount of corrosion can be measured as the amount of weight loss of the stainless steel sample. In this experiment, the weight loss of the stainless steel sample was traced using the thermobalance (sensitivity 20 μg) illustrated in figure 2. Since the iodine vapors diffuse in grease used for conventional vacuum seals, the sealing material of the contact section was wax for vacuum. A greaseless cock (using [...]* rubber packing) was used in the neck.

The experimental procedure was as described below. After installation of the stainless steel sample and the iodine crystals, the system was exhausted. At this time, the nickel disk with a hook was shifted upward using an external coil (electromagnet), and the sample was suspended outside of the reaction tube. This was followed by heating with an electric furnace, and gas removal from the reaction tube was carried out adequately at a temperature of 1100°C. In addition, the system was heated on a burner, excluding the wax seal part and the greaseless cock, and gas was removed. In this experiment, out-gas in the system must be suppressed so that the purity of the iodine vapor is not damaged since the iodine vapor pressure is low (0.05 to 0.5 mmHg). Exhaust and gas removal would be carried out until the vacuum in the system is better than 10^{-6} mmHg. Next, the set corrosion test temperature of the electric furnace would be reduced, the exhaust cock would be closed, the nickel plate disk

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would be moved downward, and the sample would be suspended in the reaction tube. After approximately two minutes, the iodine vapor would be introduced into the system, commencing corrosion. The pressure of the iodine vapor would be maintained at a suitable level by controlling the temperature of the iodine crystals. In this case, the relation between the iodine crystal temperature and the saturated vapor pressure would be based on the data of Stern et al. [13].

2.4 Experimental method on deposition of corrosion product

The corrosion product is precipitated in the low temperature part at the top of the reaction tube in the experiment in which the corrosion rate is measured. We conducted experiments using the reaction equipment with the precipitation tube in which the temperature gradually changes linearly, as illustrated in figure 5, to study this precipitation behavior in greater detail, and to gain information on the chemical form of the corrosion product. In this case, the sample was subjected to neutron irradiation using a JRR-2 pneumatic tube, and the experiments were carried out at an experimental temperature of 800°C and an iodine vapor pressure of 0.17 mmHg using radioactive AISI 316 stainless steel samples (rolled samples) which had been cooled for approximately 10 hours.

3. Experimental Findings

3.1 Corrosion rate

Table 2a illustrates the experimental results and the experimental conditions on the AISI 316 samples. Table 2b illustrates the experimental conditions and results on the AISI 304 samples. Figures 4a to 6b illustrate some of the experimental results.

3.1.1 Chronological change in corrosion rate

The initial weight loss of the sample in the experiment was greatly affected by the surface treatment and by the solution treatment of the sample. The corrosion may be suppressed or accelerated depending on the treatment. After this period, a constant corrosion period appears in which the weight loss becomes virtually constant. The rate of weight loss in this region does not depend greatly on the solution treatment nor on the surface treatment of the sample. If the temperature and the iodine vapor pressure are fixed, the corrosion rate would be virtually constant. In the following literature, the initial period of experimentation which is affected by the surface treatment is termed the initial region, while the subsequent constant corrosion period is termed the comparative region. The right columns in tables 2a and 2b illustrate the weight loss rates in the comparative region. The initial region becomes [...]* as the temperature rises, and above 900°C, the comparative region develops from virtually the start of the experiment.

The comparative region vanishes as the experiment continues for a prolonged time. The rate of weight loss gradually declines. There are cases in which the duration of the comparative region is several hours and others in which it is less than one hour. It does not always reappear.

3.1.2 Dependence of corrosion rate on iodine vapor pressure

Figure 7 illustrates the relation between the rate of weight loss in the comparative region and the iodine vapor pressure. There is some variation, but the slope is virtually one when AISI 316 is at 700°C or 900°C, as well as when AISI 304 is at 700°C. Apparently, the corrosion rate is a first order reaction proportional to the iodine vapor pressure.

3.1.3 Dependence of corrosion rate on temperature

Figure 8 illustrates the rate of weight loss in the comparative region when the iodine vapor pressure is 0.17 mmHg as a function of temperature. The weight loss rate is greatest at approximately 800°C in the case of AISI 316 stainless steel, and at 750°C in the case of AISI 304 stainless steel. At temperatures

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below 700°C, AISI 304 stainless steel has a greater weight loss rate (approximately three-fold) than AISI 316 stainless steel, but there is virtually no difference above 800°C.

3.1.4 Effect of solution treatment and of surface treatment

As discussed previously, the effects of various types of surface treatment and of solution treatment are conspicuous when the temperature is below 700°C. Virtually all experiments on samples subjected to various types of surface treatment are carried out at temperatures of 700°C and at iodine vapor pressure of 0.17 mmHg. Consequently, the observations stated below were experiments under these conditions.

(1) Effect of solution treatment

Solution treated samples and cold rolled samples were compared in the case of electro-polishing (figures 4a, b, c). In both AISI 304 stainless steel and AISI 316 stainless steel, corrosion of the solution treated samples was suppressed in the initial region. While there was a so-called induction period, the weight loss rate in the initial region in cold rolled samples was greater than that in the comparative region. This tendency was generally observed in cases in which other types of surface treatment were carried out, excluding the cases of mechanical polishing as well as of fission fragment irradiation or ion bombardment above a certain degree.

(2) Effects of surface treatment

In the current experimental range, the effects of electro-polishing and of passive state treatment have not been clearly recognized (Figs. 4a-c).

When mechanical polishing is carried out, in the case of AISI 316 solution treated samples, not only does the induction period vanish, but the weight loss in the initial pregion becomes greater than that in the comparative region (Fig.41 [15]). In the case of cold rolled samples, the weight loss is great in the initial region even with electro-polished samples, and it was not clear whether or not this tendency was assisted by mechanical polishing (Fig.4b [5]).

In the case of pickling of AISI 304 stainless steel cold rolled samples, the weight loss in the initial region is very great (Fig.4c [38]).

Figures 5a and 5b illustrate the results on solution treated samples subjected to fission fragment irradiation. In AISI 316 stainless steel, the initial induction period vanished at a fission fragment flux of 5 x 10^{14}f.f./cm^2. Conversely, the weight loss rate of the initial region was greater than that in the comparative region. This tendency was the same in samples which had been annealed for one hour at 700°C following the same degree of fission fragment irradiation. Due to fission fragment irradiation, an irradiation damage layer approximately 8 μ deep formed on the surface of the sample (weight per unit area, approximately 6.4 mg/cm^2). In Fig. 5a, the irradiation damage layer apparently began in the comparative region before removal of all corrosion since the comparative region began before the development of the weight loss of 5 mg/cm^2. When the fission fragment flux is 1.5×10^{12} f.f./cm^2, the difference from that in the case of non-irradiated samples is difficult to determine. In AISI 304 stainless steel, the irradiation effect is not as clear as in the case of AISI 316 stainless steel, but a tendency to reduction of the induction period is evident in the case of fission fragment flux of 5×10^{14} f.f./cm^2. In cold rolled samples, only one experiment was conducted with fission fragment irradiation (Fig.3b [9]), but a conspicuous effect could not be determined.

Figures 6a and 6b illustrate the effects on solution treated samples subjected to ion bombardment. The invasion depth of 1.8 MeV Ar^{++} was estimated to be approximately 0.7 μ (the amount per unit area of the irradiation damage layer was approximately 0.6 mg/cm^2). In the case of AISI 316 stainless steel, the induction period vanished when irradiation exceeding 8×10^{14} Ar^{++}/cm^2 was carried out, and the weight loss rate in the initial period was greater than that in the comparative region. However, even when the amount of irradiation was increased to 5×10^{16} Ar^{++}/cm^2, the difference from that in the case of 8×10^{15} Ar^{++}/cm^2 was not conspicuous. When the amount of irradiation was below 6×10^{14} Ar^{++}/cm^2, the difference from non-irradiated samples could not be determined. In the case of AISI 314 stainless steel, the effect was not conspicuous in the current range of irradiation.

3.2 Deposition of corrosion product

The effect of the experiments using the equipment illustrated in figure 3 was that the corrosion product precipitated in four bands in a range of temperatures of precipitation tubes of 570 to 280°C. Table 3 illustrates the colors of each precipitated material. These precipitated materials all have intense [...]* property, and identification by X-ray diffraction was not possible here since preparation of X ray samples was difficult. However, the right hand column in table 3 illustrates the chemical form surmised from the characteristics [14] of color and identification of the radioactive nuclides.

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4. Discussion

4.1 Measurement of the course of corrosion

4.1.1 Formation and properties of the corrosion product on the sample surface

In observation of the surface of samples extracted from reaction tubes before the end of the induction period during experiments on electro-polished solution treated samples at an experimental temperature of 700°C, part of the surface was seen to have undergone corrosion and to have become dark in color, while part was seen to retain the luster of electro-polishing. In addition, observation of the sample surface in the comparative region disclosed that the entire surface had become dark in color. When the samples were extracted in the air and were touched, somewhat sticky material was found on the surface. Conversely, in cold rolled samples, corrosion began over the entire surface of the sample initially, and a dark layer was observed over the surface inthe comparative region.

When corrosion begins over the entire surface of the sample, corrosion product forms over the sample surface since the rate of formation of the corrosion product is greater than the evaporation rate. This is believed to be growth. In this case, the formation rate of corrosion product is [...]* to the rate of supply of the iodine (or metal element) passing through the layer

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and with the growth of the layer since iodine is supplied to the surface of the stainless steel foundation through the corrosion product layer (or the metal element moves through this layer). Consequently, the rate falls with growth of the layer. Conversely, evaporation of the corrosion product usually occurs on the surface of the corrosion product, and assuming that it is not related significantly to the growth of the layer, the growth of the corrosion product layer is believed to stop when the formation rate and the evaporation rate reach an equilibrium. The growth itself of the corrosion product layer acts in the direction of increasing the sample weight. Consequently, assuming that growth of the corrosion product layer stops in a comparatively short time after the start of the reaction, the weight loss curve of the sample observed in this case would assume a form continuous with the comparative region after the comparatively short induction period.

The product of corrosion on stainless steel due to iodine is an iodide of Fe, Cr, Ni, Mn etc., but the chemical form when the corrosion product layer remains on the surface is believed to be that of a complex iodide of these metals. However, there is a great possibility that the chemical form during evaporation would be a single metal iodide of FeI_2, for example, under the conditions in this experiment (high temperature, low iodine vapor pressure). There are differences in the ease of evaporation when each metal element is evaporated as an iodide. Consequently, when corrosion occurs on the entire surface of the sample, there is evaporation in advance from metals which readily evaporate as iodides at the same time. Those which do not readily evaporate tend to remain on the sample surface. Specifically, the composition of metal elements in the corrosion product layer which forms on the sample surface is believed to gradually incorporate a high proportion of metals which do not evaporate. The evaporation rate overall declines since evaporation of the corrosion product occurs on the surface of the corrosion product layer. The composition of the surface of the corrosion product layer is believed to become stable as the corrosion rate and the evaporation rate of each metal element reaches an equilibrium [Note]. The great weight loss rate in the initial period in the weight loss curve of solution treated samples subjected to great surface damage and cold rolled samples, and the appearance of the

[Note] From the aforementioned discussion, the weight loss rate in the stable state would be equal to the weight loss rate of the stainless steel foundation itself, but before reaching that, there are differences between the two. However, the weight of the corrosion product layer is lower than the amount of change in the sample weight (the cause cannot lie in the induction period) in this experiment. The rate of sample weight loss is essentially unchanged from the corrosion rate.

comparative region subsequently can be explained qualitatively by the great fluctuation in the evaporation rate overall of corrosion product initially (enough to compensate the weight increase accompanying growth in the corrosion product layer).

Conversely, the induction period observed in conventional solution treated samples is believed to correspond to the fact that corrosion during the start of the experiment occurs locally and not over the entire surface of the sample (we will discuss below the reasons for local occurrence of corrosion). However, in this case also, if the corrosion region expands over the entire surface, the subsequent course of corrosion would be identical to that in the case of cold rolled samples, and a constant corrosion product layer would form on the surface. The fact that the weight loss rate in the comparative region is not dependent on the type of surface treatment nor on the solution treatment of the sample is explained by the existence of such a constant corrosion product layer, and by the fact that the weight loss rate is the same rate as the evaporation rate from the surface of the corrosion product layer.

As seen in figure 8, the weight loss rates in the comparative region for AISI 316 and AISI 304 differ below 700°C. A 2% content of Mo in AISI 316 does not readily evaporate as iodide when the iodine vapor pressure is 0.1 mmHg at a temperature of approximately 700°C [14]. Consequently, in the case of AISI 316 stainless steel, the content of Mo on the surface of the corrosion product layer which forms on the sample surface under these conditions is far greater than 2%. Consequently, the evaporation rate overall from the surface of the corrosion product layer of AISI 316 is believed to be far lower than that in the case of AISI 304 stainless steel.

The chemical form of the principal precipitate which precipitates in the low temperature region of the reaction tube of the thermobalance was estimated from the results of precipitation behavior experiments. As illustrated in table 3, the form is believed to be MI_2. M is the metal element. If the chemical form of the iodide precipitating from the surface of the corrosion product layer of the surface of the sample is MI_2, the chemical form of the surface of the corrosion product layer in this case would not be MI_2. The reason is as follows. If the chemical form of the surface of the corrosion product layer were Mi_2, the evaporation rate would be constant independently of the iodine vapor pressure. However, as figure 7 indicates, the weight loss rate (and the evaporation rate proportional to this) in the comparative region at 700°C is proportional to the iodine vapor pressure. Consequently, the chemical form of the surface of the corrosion product layer is not Mi_2, but is probably the iodide of the order below MI_2.

When the corrosion temperature is raised above 700°C, the initial region becomes gradually shorter as described above, and when the temperature exceeds 900°C, the comparative region develops from the start of the experiment in all samples. This phenomenon is believed to be because the evaporation rate of the corrosion product layer at such high temperatures becomes great, and the corrosion product layer either essentially ceases to form, or it becomes a constant layer (very thin layer) in a short time if it does form. An additional cause is believed to be that corrosion occurs on the surface of the sample at the same time that the experiment begins in solution treated samples. Actual observation of the surface of AISI 304 stainless steel samples in the comparative region at 900°C reveals that the color is grey, which differs from the color at 700°C. Material which seems to be corrosion product layer was not outwardly evident. However, in the case of AISI 316 stainless steel samples, black powdery material was seen on the surface. This black powder is surmised to be the remains of the powder of metals such as Mo which do not readily form iodides at such a temperature. When the temperature exceeds 800°C, this black powder is believed to exist in a form which does not readily block the evaporation of corrosion product layer or the reaction between iodine and the sample foundation since there is virtually no difference in the weight loss rates in the comparative region between AISI 316 stainless steel and AISI 304 stainless steel.

The comparative region vanished when experiments are continued for prolonged periods. The cause of the decline in the weight loss rate is believed to be the accumulation of metal elements and non-metallic elements which do not readily evaporate as iodides on the surface. However, out-gas accumulates in the thermobalance system, the purity of the iodine vapor declines, and the corrosion product layer degenerates.

4.1.2 Cause of appearance and disappearance of induction period

The induction period which appears characteristically in solution treated samples is believed to be due to local corrosion at the start of the experiment, as indicated previously. However, there are two explanations as to why corrosion occurs locally and why corrosion occurs over the entire surface when great damage is inflicted on the surface.

The first is believed to be damage due to the formation of an oxide layer on the surface. An oxide layer is believed to exist on the surface when the sample has been subjected to solution treatment, or when the surface is in the state following passive state treatment. In addition, in the case of electropolishing, a thin oxide layer (approximately 10 Å) is known to form [15]. These oxide layers become protective layers for iodine. Corrosion is explained as occurring locally from regions in which the protective layer is thin (damaged), and then expanding from there. In this case, the diasappearance or contraction of the induction period due to ion bombardment, mechanical polishing or fission fragment irradiation is believed to be due to damage resulting from the elimination of the oxide layer. Moreover, when the temperature is raised above 900°C, the effect of the protective layer is virtually lost, and the induction period vanishes. The effects of fission fragment irradiation and of ion bombardment differ greatly in AISI 316 stainless steel and AISI 304 stainless steel. (Figs. 5a, 5b, 6a and 6b) illustrate the differences in the properties of both oxide layers. This is believed to be because the AISI 304 stainless steel oxide layer is damaged less by irradiation.

However, the induction period does not appear even with passive state treatment or electro-polishing in the case of cold rolled samples. In contrast, in commencing with these experiments, when the sample temperature was raised from room temperature to the experimental temperature (for example 700°C), the surface form became instable due to annealing during working deformation. This is explained by the loss of density in the oxide layer which forms during passive state treatment and during electro-polishing. Thus, cold rolled samples (in short, the working deformation which should be annealed at 700°C in these samples was temporarily annealed) which had completed the corrosion experiments at 700°C (approximately two hours) were subjected to electro-polishing again, and when corrosion experiments were repeated, the induction period was not observed, as expected. Consequently, if the oxide layer of the solution treated sample were caused by the induction period, the oxide layer of the cold rolled samples would differ from that of solution treated samples, and the oxide layer itself would not be dense, or it would not withstand heat treatment. [However, when commencing the corrosion experiment on cold rolled samples as an extra experiment, one atmosphere pressure of air is introduced into the system for several minutes before the introduction of iodine vapors in the thermobalance system, and an oxide layer (estimated thickness approximately 1 μ) is formed on the surface of the sample in the reaction tube at 700°C. Subsequently, when experiments were carried out at 700°C, corrosion virtually did not take place (within two hours in the experiment). Consequently, there are also cases in which the oxide layer which forms under certain conditions in cold rolled samples as well is very effective as the protective layer.]

The second explanation for the appearance and disappearance of the induction period is the start of corrosion from a certain part of the defect on the crystal structure on the surface of the sample foundation. Specifically, the defective section is believed to be an active point in relation to corrosion due to iodine vapors, and corrosion is believed to start and spread using this active point as the nucleus. The defective part is believed to contain a crystalline boundary or inversion, impure atoms, precipitates etc.). There are great differences in the surface density of the defective part of cold rolled samples and solution treated samples, beginning with crystalline boundaries. In cold rolled samples, the density becomes greater as the apparent surface corrosion progresses, while in solution treated samples, it becomes lower as localized corrosion occurs. In addition, the conduct of mechanical polishing of solution treated samples, and the reduction or disappearance of the induction period following fission fragment irradiation or ion bombardment, of course, is due to the formation of many crystal defects on the surface, and to an increase in the density of the active points, depending on the treatment. In addition, the difference in the irradiation effect between AISI 316 stainless steel and AISI 304 stainless steel is due to the difference in the ease of annealing (at the corrosion temperature) or to the ease of irradiation damage. Moreover, the shortening or disappearance of the induction period as the temperature of solution treated samples rises is due to overall corrosion resulting from corrosion in parts lacking defects due to thermal [...]*.

The bases for determining which of the above two explanations is correct, or if either of them is correct, have not been determined in the current experiments. However, if the oxide film of the solution treated sample is the cause of the induction period, the oxide films which form during solution treatment, electro-polishing or passive state treatment would be expected to have different modes of appearance of the induction periods in the samples subjected to those treatments. However, there is little difference in the mode of appearance of the induction periods, as seen in figure 4a. This indicates that the second explanation is comparatively effective.

In the case of cold rolled samples, even when corrosion occurs over the entire surrace of the sample without an induction period, differences in the density at the point of commencement of corrosion would be expected to occur due to treatment of the sample. The appearance of differences in the mode of weight loss (the period of the initial region, the weight loss rate etc.) in the initial region due to surface treatment could be explained as corresponding to this, but in addition, there are also cases in which unevenness appears on the surface of the sample due to treatments, and in which the surface area increases. Detailed examinations of the individual cases are essential.

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4.2 Removal probability

Rosner et al. [16] have defined the removal probability Q as the scale of reactivity at high temperatures of fluorine gas and of chlorine gas on metals. Q is expressed by the following equation.

$$Q \equiv E/Z$$

Here, Z represents the collision rate (atoms/sec/cm^2) of halogen atoms such as fluorine on the metal surface. E represents the evaporation rate (atoms/sec/cm^2) of metal elements. Specifically, Q is the probability of evaporation of one metal element as a halogen compound following the collision of one halogen atom on the surface of metal. If Q is known, for example, if Z were calculated from the halogen concentration, gaseous phase pressure and temperature etc. in a reaction of metal with halogen in an inert gas, E, specifically the rate of corrosion·removal of metals, could be calculated (excluding those cases in which the corrosion product which had evaporated has dissociated in the gaseous phase, with the metal elements reverting to the metal surface).

Following the low of gas kinematics, Z can be calculated by the following equation.

$$Z = 3.51 \times 10^{22} \cdot P/\sqrt{M \cdot T} \quad (\text{atoms/sec/cm}^2)$$

Here, P is the pressure (mmHg), M is the amount of molecules of gas and T is the temperature (°K). Based on the above equation, the experimental results illustrated in figure 8 are expressed by Q in figure 9. Under these experimental conditions, iodine vapor need not always be present only in the form of I. There are cases in which it could exist as I_2. Thus, we calculated the mole fraction (figure 10) of I and of I_2 based on literature [14], and computed Z as a result. Moreover, in computing E, we used the mean values of weight for Fe, Ni, Cr, Mo and Mn as the equivalent molecular amounts of the metal elements. Q reaches a peak at approximately 800°C in AISI 316 stainless steel, and at 750°C in AISI 304 stainless steel similarly to the rate of weight loss. With the rise in temperature, the proportion of gaseous iodine atoms with the activation energy required for producing reaction products increases, but at still higher temperatures, the dissociation rate of the reaction product increases, and the reaction product dissociates without evaporation in that chemical form. Thus, the emission rate of iodine increases [14]. For that reason, there is a temperature at which the evaporation rate of the reaction product reaches a peak. Specifically, this is the peak temperature for Q also.

The value of Q in figure 9 is the value when the iodine vapor pressure is 0.17 mmHg, but when the temperature exceeds 700°C, the iodine vapor exists virtually only in the form of I. Moreover, at temperatures above 700°C, even when the iodine vapor pressure is below 0.17 mmHg, the value of Q in figure 9 could be applied as is considering that the corrosion rate is virtually proportional to the iodine vapor pressure, as seen in figure 7.

However, the results illustrated in figure 9 refer to Q in the comparative region. Below 700°C, one must note that the weight loss rate in the initial region differs considerably from that in the case of the comparative region, as already indicated. In the case of cold rolled samples and solution treated samples which had been injured greatly on the surface, Q becomes very great, as illustrated in figure 9, in the initial period of corrosion. The temperature at which Q reaches a peak shifts to a lower temperature. In addition, when corrosion occurs simultaneously with fission fragment irradiation as inside actual cladding, this tendency becomes greater than in the case of experiments following irradiation. In this sense, the necessity of experiments under irradiation is great.

5. Summary

1. We have studied the corrosion of AISI 316 and AISI 304 stainless steel due to iodine vapor in the iodine vapor pressure range of 0.05 to 0.5 mmHg and at temperatures of 500°C to 1000°C using thermobalances. We studied the effects of solution treatment of stainless steel as well as the effects of surface treatments such as electro-polishing, passive state treatment, pickling, mechanical polishing, fission fragment irradiation and ion bombardment on corrosion. In addition, we observed the evaporation and precipitation behavior of corrosion products.

2. The weight loss rate of samples in the initial period of corrosion was affected by solution treatment of the samples and by surface treatment, and it exhibited an induction period due to treatment. Conversely, while corrosion accelerated, a constant corrosion region appeared in this period during which the weight loss rate was virtually constant. The weight loss rate in this region was not greatly affected by treatment of the sample. The constant corrosion region vanished as the reaction proceeded, and the rate of weight loss gradually declined. The effects of various treatment in the initial period of corrosion became less conspicuous as the temperature rose. Above 900°C, a constant corrosion region developed from the start of the experiment.

3. The rate of sample weight loss in the constant corrosion region was virtually proportional to the iodine vapor pressure at temperatures above 700°C for both AISI 316 and AISI 304 stainless steel. This is apparently a first order reaction.

4. The rate of sample weight loss in the constant corrosion region reached a peak at 800°C in the case of AISI 316 stainless steel, and a peak at 750°C in the case of AISI 304 stainless steel. At temperatures below 700°C, the rate for AISI 304 stainless steel was approximately three times as great as the rate for AISI 316 stainless steel. However, above 800°C, there was virtually no difference between the two.

5. At 700°C, in the case of solution treated samples, an induction period was conspicuous early in corrosion. This was similar in cases of electro-polishing and passive state treatment of the surface. However, when the surface was subjected to mechanical polishing, fission fragment irradiation or ion bombardment above a certain degree, the induction period vanished, and corrosion accelerated early in the corrosion period, or the induction period was reduced. The effects of fission fragment irradiation and of ion bombardment were more pronounced in the case of AISI 316 stainless steel than in the case of AISI 304 stainless steel. In the case of cold rolled samples, the induction period did not appear. Rather, the rate of weight loss early in the corrosion period increased. In addition, this tendency did not change due to surface treatment in the range of this experiment.

6. At temperatures below 700°C, a corrosion product layer was observed on the surface of the sample. The evaporation of the corrosion product layer occurred from the surface of this layer. This is believed to conform to the development of uniform rates of formation and of evaporation of the corrosion product layer, as well as to regions in which the the formation of the corrosion product layer occurs through a constant reaction. The composition of the metal elements in the constant corrosion product layer is proportional to the composition in stainless steel. The proportion of metals forming iodides which do not readily evaporate is believed to be great.

7. The great weight loss rate in the initial period of corrosion in cold rolled samples is due to corrosion over the entire surface of the sample at the start of the experiment, as well as to the dominant evaporation of metal elements which readily evaporate as iodides in the process until the constant formation of the corrosion product layer.

8. The induction period which appears in the samples which have been subjected to solution treatment is believed to correspond to local corrosion on the surface of the sample at the start of the experiment. There are believed to be two possible causes of this local corrosion: 1), An oxide on the surface has a protective effect toward iodine. This effect is great in the case of solution treated samples. 2) Corrosion begins with crystal

borders, working deformation or irradiation damage which serve as the nuclei for certain sections in which there are crystal defects on the surface of the sample. In the case of solution treated samples, the surface density at such points where corrosion begins is low.

9. The corrosion products are precipitated at low temperature sections (in the temperature range of 570°C to 280°C) of the reaction tube, and their chemical forms are surmised to be NiI_2, CrI_2, FeI_2 and MnI_2.

Postscript

In these experiments, we have dealt with various surface treatments which are factors affecting the corrosion rate, but these were somewhat diverse, and observation of the effects of the individual surface treatments was conducted only partially. In addition, estimation of the corrosion mechanism could only be carried out qualitatively. In the future, observation of the structures of the surfaces of the stainless steel sample foundations and of the changes in the sturcutres using XMA and [...]* are indispensible for quantitative study of the effects of various surface treatments and their causes, or of the corrosion mechanism, especially the corrosion mechanism in the initial period of corrosion in which the effects of the surface treatment are extreme. Detailed research must be carried out on each surface treated sample. At a temperature of approximately 700°C, the sensitization phenomenon accompanying precipitation of carbides is known to occur. When experiments are carried out for prolonged periods, structural observation would be indispensible in this sense. However, the corrosion product layer which forms on the surface of stainless steel (perhaps, low grade iodides) is not always stable in the air (probably due to deliquesence), and in preparing samples for the microscope, techniques would be essential for fixation of the layers or for their removal.

We have noted in the current experiment that there are cases in which the corrosion rate is greatly affected by irradiation damage. From this, it is clear that there are cases in which the corrosion rate varies in samples subjected to some sort of deformation or stress in their crystalline structure. In this sense, research is essential into corrosion when great mechanical stress is imposed, as in actual reactor cladding. In addition, research must be carried out focusing on stress corrosion cracks.

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Tables and Figures

Table 1. Chemical analysis of samples (%).

	Cr	Ni	Mo	C	Si	Mn	P	S	Cu
AISI 304	18.2	9.14	0.14	0.06	0.51	1.15	0.03	0.011	0.16
AISI 316	17.1	12.0	2.23	0.07	0.65	1.56	0.03	0.005	0.34

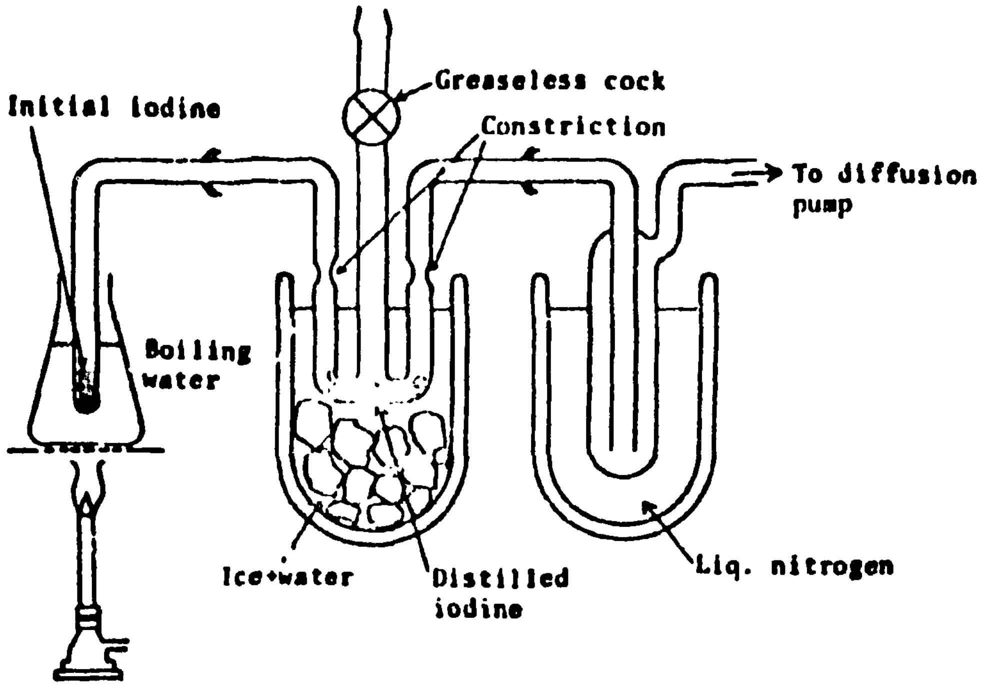

Fig. 1. Apparatus for distillation of iodine

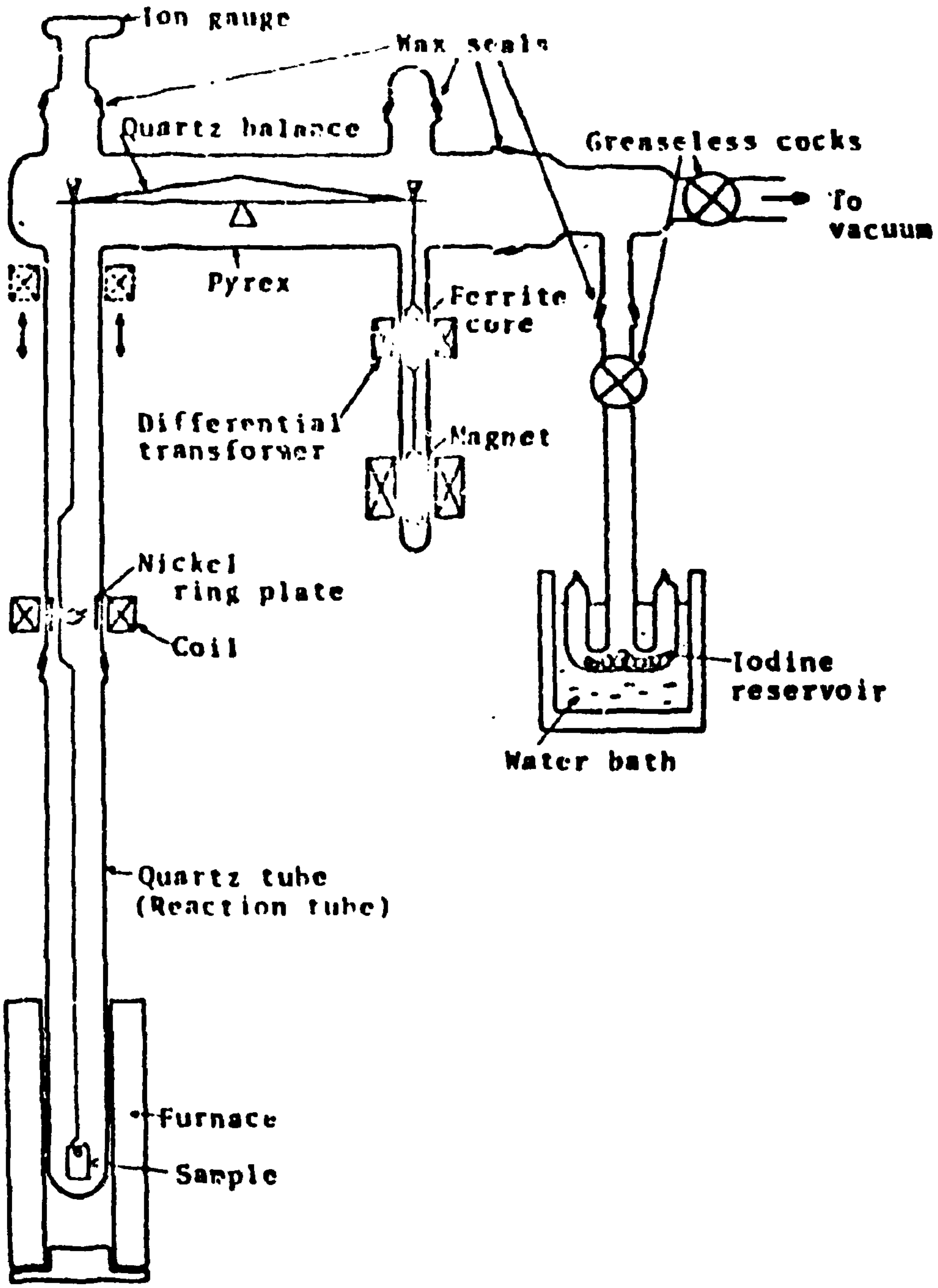

Fig. 2. Thermobalance for corrosion test with iodine vapour.

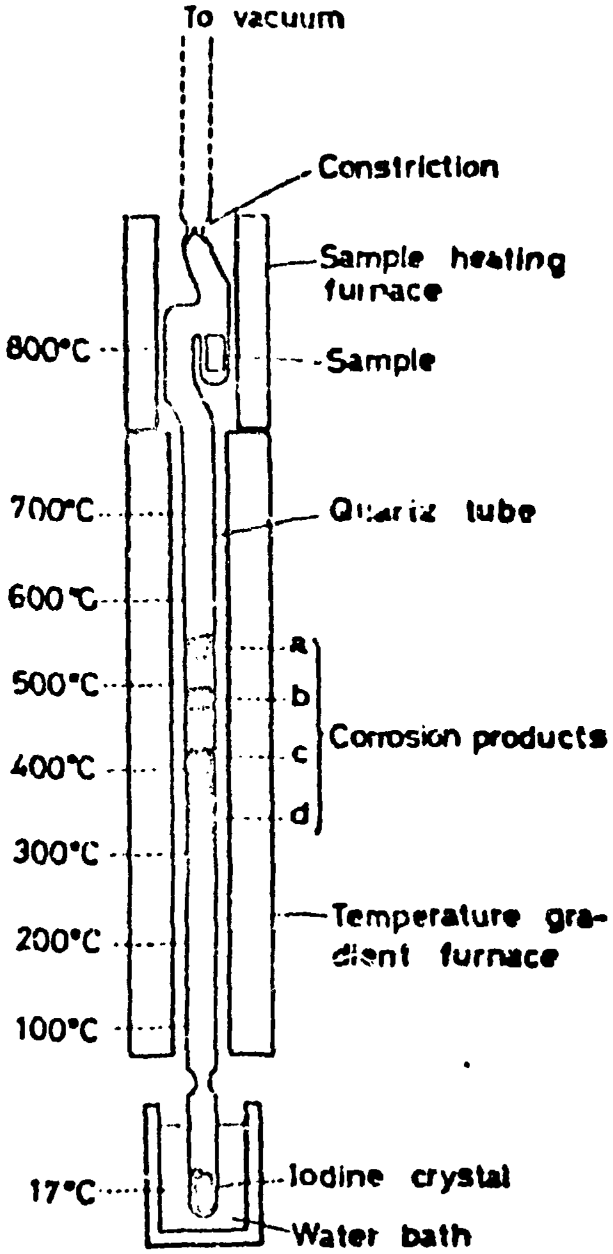

Fig. 3. Deposition of corrosion products in thermal gradient tube

Table 2a. Experimental data for AISI 316 stainless steel.

Run No.	Corrosion temperature (°C)	Iodine crystal temperature (°C)	Heat treatment of sample	Surface treatment of sample	Mode of initial corrosion	Weight loss rate $(mg/cm^2/min)$
1	500	17	AR	nothing	LIN	5.2[illegible] $\times 10^{-4}$
2	600	17	AR	nothing	LIN	2.38×10^{-2}
3	600	17	ST	nothing	IND	2.60×10^{-2}
4	700	4	AR	nothing	ACC	2.73×10^{-2}
5	700	17	AR	nothing	ACC	$9.$[illegible] $\times 10^{-2}$
6	700	17	AR	EP	ACC	9.92×10^{-2}
7	700	17	AR	PV	ACC	7.44×10^{-2}
8	700	17	AR	MP	ACC	$8.$[illegible] $\times 10^{-2}$
9	700	17	AR	EP+FF(5×10^{14} ff/cm^2)	ACC	1.08×10^{-1}
10	700	17	ST	nothing	IND	1.06×10^{-1}
11	700	17	ST	EP	IND	7.76×10^{-2}
12	700	17	ST	EP	IND	1.02×10^{-1}
13	700	17	ST	EP	IND	8.18×10^{-2}
14	700	17	ST	PV	IND	8.53×10^{-2}
15	700	17	ST	EP+MP	ACC	1.02×10^{-1}
16	700	17	ST	EP+FF(1.5×10^{12} ff/cm^2)	IND	1.08×10^{-1}
17	700	17	ST	EP+FF(1.5×10^{12} ff/cm^2)	IND	8.65×10^{-2}
18	700	17	ST	EP+FF(5×10^{14} ff/cm^2)	ACC	8.20×10^{-2}
19	700	17	ST	EP+FF(5×10^{14} ff/cm^2)*	ACC	9.83×10^{-2}
20	700	17	ST	EP+ION(7×10^{13} Ar/cm^2)	IND	7.98×10^{-2}
21	700	17	ST	EP+ION(6×10^{14} Ar/cm^2)	IND	8.11×10^{-2}
22	700	17	ST	EP+ION(8×10^{15} Ar/cm^2)	ACC	8.00×10^{-2}
23	700	17	ST	EP+ION(5×10^{16} Ar/cm^2)	ACC	7.50×10^{-2}
24	700	30	AR	nothing	ACC	2.48×10^{-1}
25	800	17	AR	EP	ACC	2.53×10^{-1}
26	800	17	ST	nothing	IND	2.78×10^{-1}
27	900	4	ST	EP	LIN	4.17×10^{-2}
28	900	10	AR	EP	(ACC)	8.93×10^{-2}
29	900	17	AR	nothing	LIN	1.69×10^{-1}
30	900	17	AR	EP	LIN	1.59×10^{-1}
31	900	17	ST	EP	(LIN)	1.39×10^{-1}
32	900	27	AR	nothing	LIN	3.35×10^{-1}
33	1000	17	AR	EP	LIN	6.35×10^{-2}

For explanation of characters in this table, see annotations under Table 2b.

Table 2b. Experimental data for AISI 304 stainless steel.

Run No.	Corrosion temperature (°C)	Iodine crystal temperature (°C)	Heat treatment of sample	Surface treatment of sample	Mode of initial corrosion	Weight loss rate (mg/cm²/min)
34	500	17	AR	EP	LIN	1.74×10^{-3}
35	600	17	AR	EP	LIN	7.19×10^{-2}
36	700	4	ST	nothing	IND	8.93×10^{-2}
37	700	17	AR	EP	LIN	3.72×10^{-1}
38	700	17	AR	PC	ACC	4.36×10^{-1}
39	700	17	ST	nothing	IND	3.23×10^{-1}
40	700	17	ST	EP	IND	2.78×10^{-1}
41	700	17	ST	EP+FF(1.5×10^{12} ff/cm^2)	IND	3.49×10^{-1}
42	700	17	ST	EP+FF(5×10^{14} ff/cm^2)	IND	3.65×10^{-1}
43	700	17	ST	EP+FF(5×10^{14} ff/cm^2)*	IND	3.26×10^{-1}
44	700	17	ST	EP+ION(7×10^{13} Ar/cm^2)	IND	3.04×10^{-1}
45	700	17	ST	EP+ION(6×10^{14} Ar/cm^2)	IND	2.96×10^{-1}
46	700	17	ST	EP+ION(8×10^{15} Ar/cm^2)	IND	2.93×10^{-1}
47	700	17	ST	EP+ION(5×10^{16} Ar/cm^2)	IND	2.70×10^{-1}
48	700	30	ST	nothing	IND	7.29×10^{-1}
49	800	17	AR	EP	LIN	3.42×10^{-1}
50	900	17	AR	EP	LIN	1.88×10^{-1}

AR : As cold-rolled.
ST : Solution treatment (1100°C, 1hr).
EP : Electro-polishing (H_3PO_4-H_2SO_4-CrO_3 sol.).
PV : Passive state treatment [50%H_2SO_4(70°C,5min) and 50%HNO_3(in boiling,1hr)].
MP : Mechanical polishing (#800 emery-paper).
PC : Pickling (20%HNO_3-2%HF).
FF : Fission-fragment irradiation.
ION : Ion-bombardment (1.8 MeV-Ar^{++}).
ACC : Acceleration.
IND : Induction.
LIN : Linear corrosion
*(annealed at 700°C for 1hr in vacuum after irradiation).

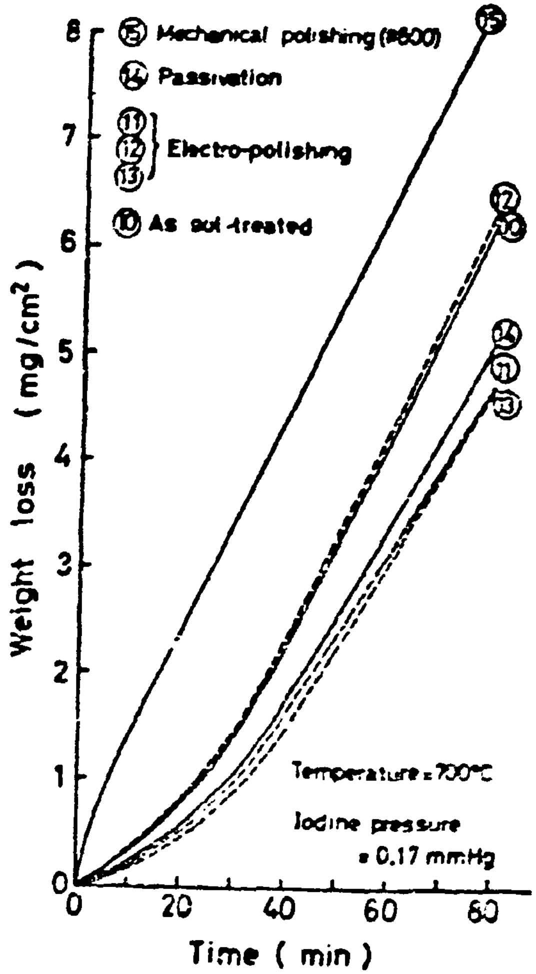

Fig. 4a. Effect of surface treatment on corrosion with iodine vapour for solution-treated AISI 316 stainless steel.

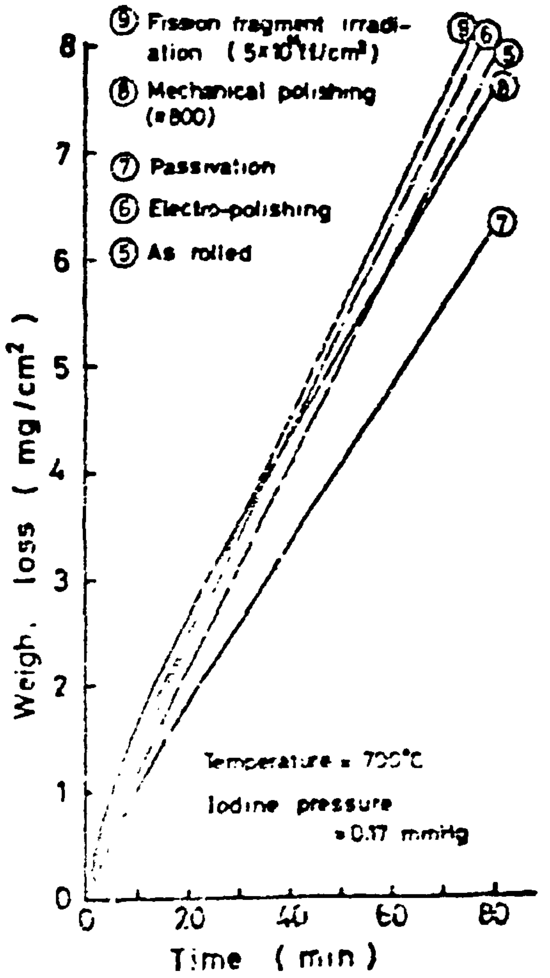

Fig 4b Effect of surface treatment on corrosion with iodine vapour for cold-rolled AISI 316 stainless steel

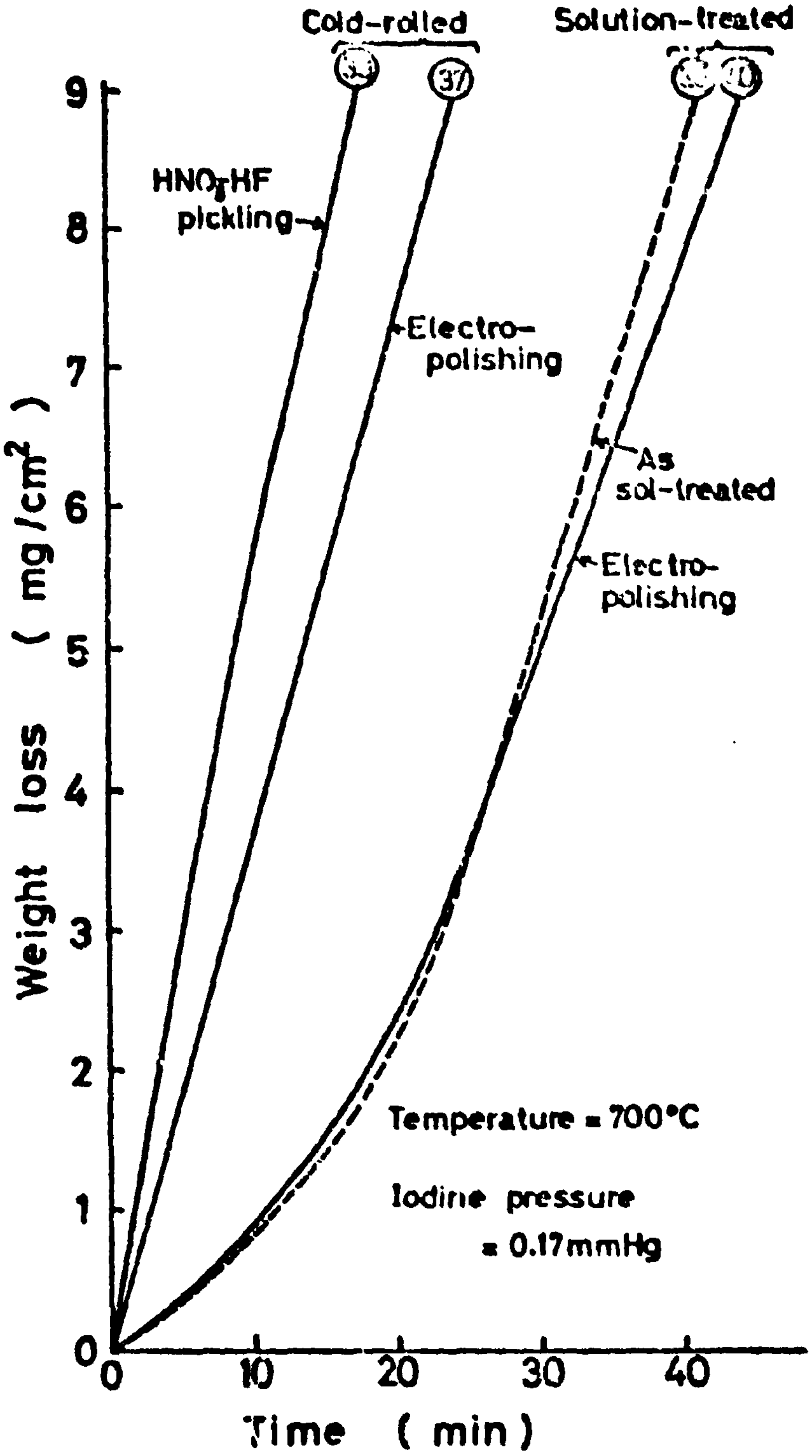

Fig. 4c. Effect of surface treatment on corrosion with iodine vapour for AISI 304 stainless steel

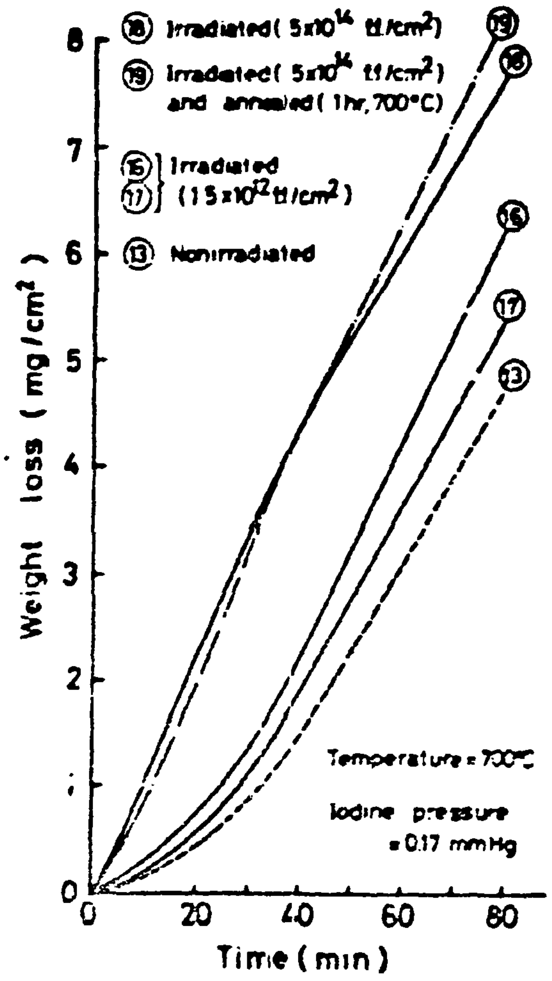

Fig. 5a. Effect of fission-fragment irradiation on corrosion with iodine vapour for solution-treated and electro-polished AISI 316 stainless steel

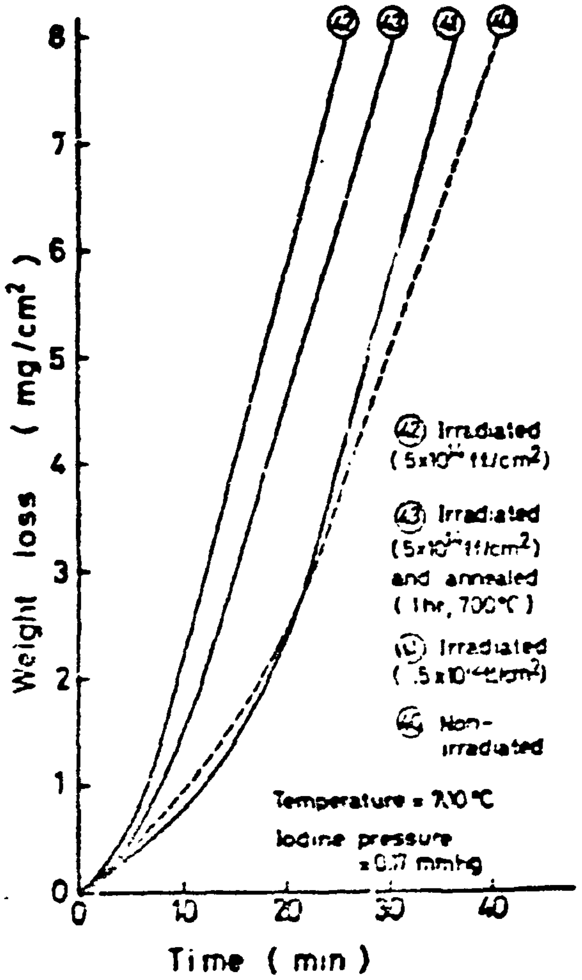

Fig. 5b. Effect of fission-fragment irradiation on corrosion with iodine vapour for solution-treated and electro-polished AISI 304 stainless steel

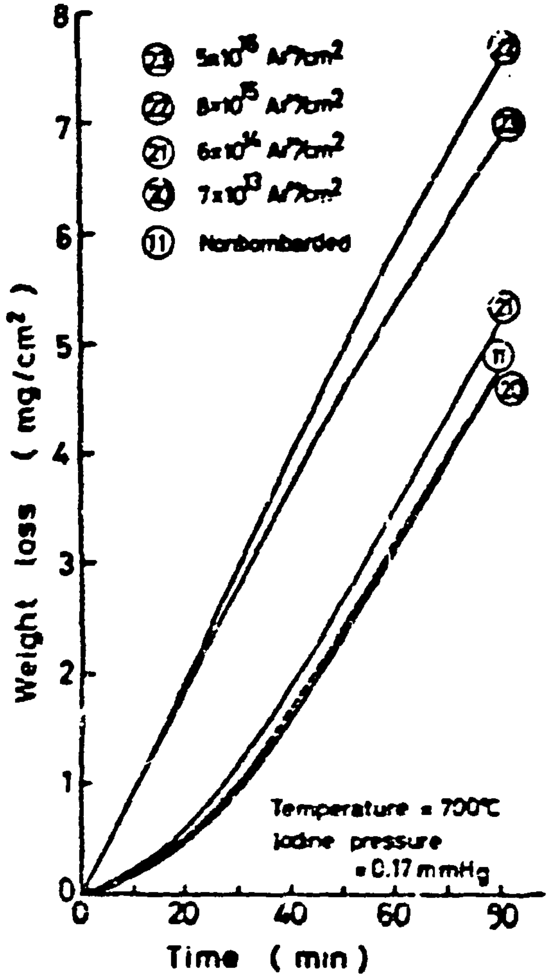

Fig. 6a. Effect of ion-bombardment on corrosion with iodine vapour for solution-treated and electro-polished AISI 316 stainless steel

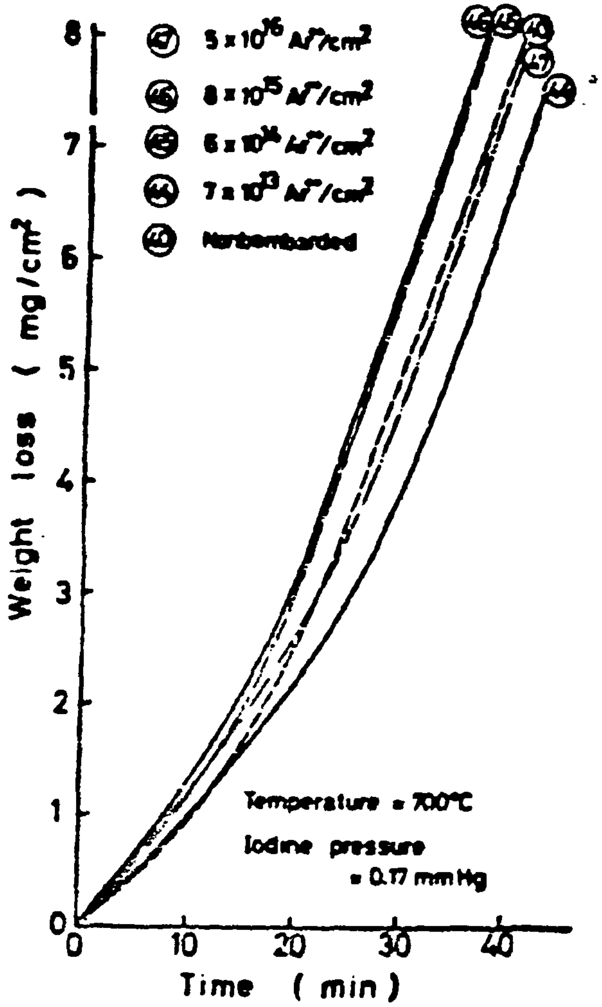

Fig. 6b. Effect of ion-bombardment on corrosion with iodine vapour for solution-treated and electro-polished AISI 304 stainless steel

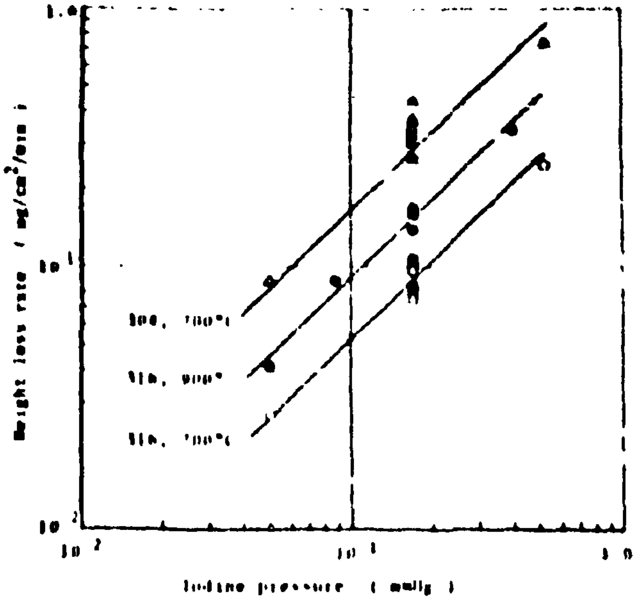

Fig. 7 Iodine vapour pressure dependence of corrosion rate for AISI 316 and AISI 304 stainless steel.

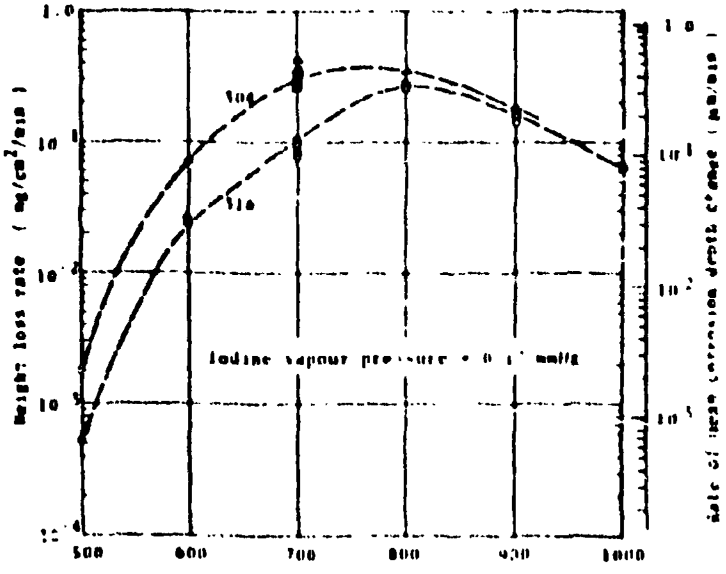

Fig. 8. Temperature dependence of corrosion rate with iodine vapour for AISI 316 and AISI 304 stainless steel.

Table 3. Deposition behavior of corrosion products in thermal gradient tube of quartz.

	Deposition temperature	Order in abundance	Colour	Solubility in water	Active nuclide	Probable iodide
a	570 ~ 510°C	2	Brown	readily	^{51}Cr	NiI_2, CrI_2
b	500 ~ 460°C	3	Brown	readily	^{56}Mn	MnI_2
c	440 ~ 410°C	4	Dark green	readily	(^{56}Mn)	?
d	400 ~ 280°C	1	Reddish purple	readily	-	FeI_2

Sample : AISI 316 irradiated in a thermal reactor (nvt= $6 \times 10^{16} n/cm^2$) and cooled for 10 hr.

Temperature : 800°C

Iodine vapour pressure : 0.17 mmHg

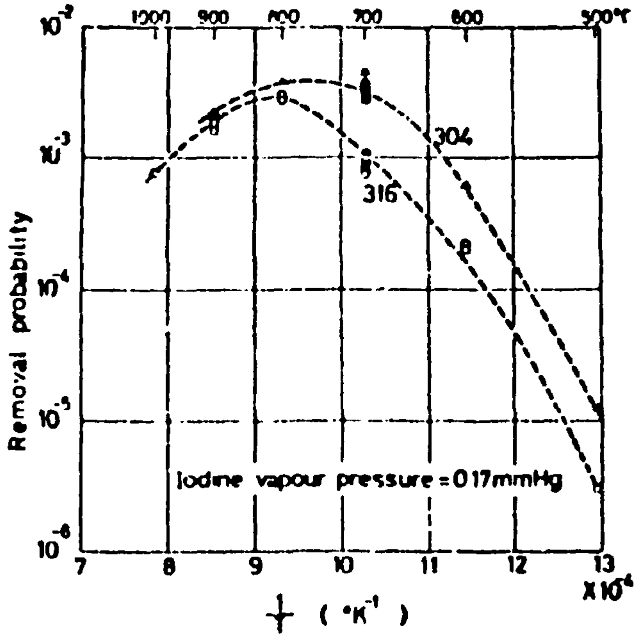

Fig 9 Removal probability* vs temperature

$* = \frac{\text{Evaporation rate of metal(atoms/cm}^2\text{/sec)}}{\text{Collision rate of iodine (atoms/cm}^2\text{/sec)}}$

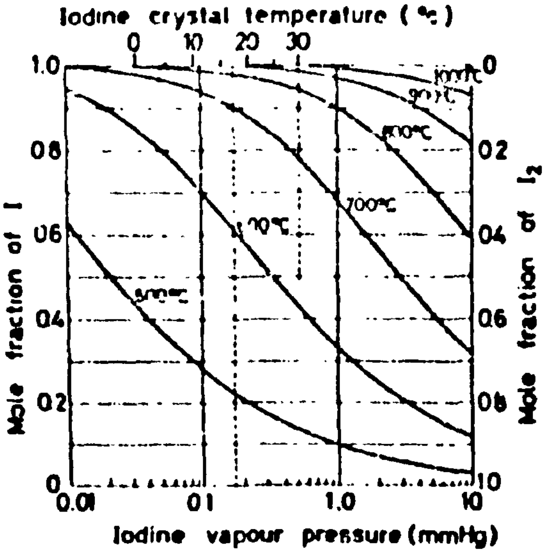

Fig 10 Mole fraction of I or I_2 in iodine vapour as a function of pressure and temperature (calculated from the data by reference-14))