On the Corrosion of Fe-2%C-Al Alloys in Atmospheric Sulfur Vapor at 900°C*

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Synopsis

2wt%C-cast iron containing aluminum (up to 25wt%Al) were corroded under an atmospheric pressure of sulfur vapor at 900°C up to 10 hr, in order to clarify the detailed mechanism of the corrosion of these alloys. Alloys with less aluminum content (1 to 4wt%Al) having nodular graphitic substrate showed the greater corrosion obeying a linear rate law and the very anomalous scale growth of an inner layer was shown. Furthermore, with more aluminum (>7wt%Al) the corrosion kinetics was nearly parabolic, but after some time of corrosion they showed the so-called "break away." Their total scales were very thin and also without corner scale, but still the inner layer was very thicker than the outer one. From the above observations and the marker position found at the outer/inner layer interface, most of the scale was concluded to form with the inward migration of sulfur vapor through the scale which was very porous with graphite particles and other sulfides as well as pyrrhotite.

I. Introduction

The addition of aluminum to cast iron as well as pure iron and steel has been found to increase markedly the resistance to sulfur attack from the results of previous studies¹⁻³⁾ and also our observations.^{4,5)} However, those results being mainly for the corrosion test of industrial materials, there are many ambiguous points about the details of the kinetics of sulfurization and its mechanism.

From the above points of view, in this investigation the alloys specially prepared were used to clarify the details of the corrosion of cast iron (2wt%C) containing aluminum (0 to 25wt%) in the atmospheric sulfur vapor at 900°C.

As has been reported,⁶⁾ graphitization in cast iron is easily proceeded by the addition of aluminum in some range of concentration, but in other content there is no such a tendency, so that the mechanical properties as well as the structure are much influenced by the morphology of carbon in the matrix.

In this paper, some characteristic features of the corrosion product (scale) formed on these alloys were indicated and the mechanism of such scaling was discussed with the observations in relation to the carbon morphology in the matrix.

II. Experimental

1. Test Pieces

The alloys used in this experiment were prepared with melting electrolytic iron, pure aluminum and graphite in a high-purity alumina crucible by means of a high-frequency induction furnace and chill-casting in the cast iron mould into a slab. Table I shows the notation of alloys and their chemical compositions, and also the stable phases in each alloy at 900°C.

As these as-cast alloys were found to have the considerable growth of graphitization during heating in some concentration range of aluminum, as stated before, the following stabilizing heat-treatment was carried out before using as corrosion test pieces.

Under an atmosphere of an order of 10^{-3} mmHg these slabs were heated up to 900°C at a rate of 4°C/min and after keeping them at that temperature for 3.5 hr they were cooled down to the room temperature at the same rate as that of heating. This cyclic thermal process was carried out once for the slabs like 200, 213, 217, 219, and 225, while twice for 201, 203, 204, and 207. By these heat-treatments the growth of the test pieces decreased down to within almost 0.5% as has been reported.⁶⁾

From these heat-treated slabs the test pieces were cut into a size of 5×9×13 mm and polished up to No. 1000 emery paper and then rinsed with water and alcohol followed by degreasing with trichlorethylene.

2. Apparatus and Procedure

Heating furnaces for the corrosion experiment and evacuated ampoule contained a test piece and sulfur were shown in Fig. 1. The furnaces consist of two, the upper one being a corrosion furnace kept at 900° ±3°C, and the lower a sulfur furnace kept at the boiling point of sulfur (445°C) in order to keep the sulfur vapor under 1 atm.

The corrosion process was proceeded as follows:

Table 1. Alloy number and chemical composition of alloys and their present phases at 900°C
 γ : austenitic phase, α : ferritic phase, C: graphite, K: Fe-Al-C compound

Alloy number	200	201	203	204	207	210	213	217	219	225
C (wt%)	2.05	2.07	2.01	2.04	1.92	2.10	2.03	2.20	1.96	2.08
Al (wt%)	0.45	1.54	2.86	4.56	7.02	9.85	11.50	17.90	19.96	25.20
Phase	$\gamma+C$	$\gamma+C$	$\gamma+C$	$\gamma+C$	$\gamma+K$	$\alpha+K$	$\alpha+K$	$\alpha+K$	$\alpha+K$	$\alpha+C$

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Fig. 1. Schematic presentation of experimental apparatus and its arrangement

some amount of sulfur was contained into the (B) part in a quartz ampoule shown in Fig. 1 and the test piece was hung up at the (A) part by means of Kanthal or platinum wire. Then the ampoule was evacuated through the (C) part up to 4×10^{-6} mmHg and sealed at that part. The ampoule was designed in order that the position of sulfur as well as a test piece would be at an optimum zone of each furnace. Moreover, the (A) part of the ampoule was made of a transparent quartz tube so as to look at the appearance of the test piece inside the ampoule during and after corrosion. The corrosion time was taken from the insertion of the ampoule into the furnaces from the top up to the quenching the ampoule in iced brine after each run.

After the corrosion process the surface appearance of the test piece was observed and then the scale morphology and its growth as well as the decrement of substrate were measured in the sectioned test piece.

III. Experimental Results

1. Corrosion Rate

Figure 2 shows the change in corrosion behavior with time at 900°C under an atmospheric pressure of sulfur vapor, where the amount of corrosion was estimated from the decrement of thickness at one side of a test piece, because of the irregularity of scale thickness among alloys as stated later. From this figure it is understood that alloys with more aluminum content than that of 207 showed less corrosion rate than the alloy without aluminum (200), but alloys with less aluminum content (for example, 201, 203, and 204 alloys) showed much more corrosion than 200 alloy. Furthermore, alloys with less aluminum content (except 200) showed rather a corrosion tendency of about linear rate law, whereas with the increase of aluminum content, alloys seemed to obey generally a parabolic rate law, though they suffered the so-called "break away," that is, the sudden in-

Fig. 2. Decrement of thickness of substrate of each alloy with time. Numbers in the figure indicate the alloy number.

Fig. 3. Change in corrosion behavior of Fe-2%C alloys with aluminum content as well as Fe-Al alloys. The alloys were exposed to an atmospheric pressure of sulfur vapor at 900°C for one hour.

crease of corrosion after some time.

Accordingly, since it is difficult to calculate the corrosion rate constant based on such as a unique law, the corrosion amount per 1 hr at the beginning of corrosion was plotted against the aluminum content of alloys in Fig. 3, where for a comparison the results from Fe-Al alloys were also reproduced in the same figure which has shown to obey a parabolic rate law under the same experimental condition.⁵⁾ From the figure the corrosion of cast iron containing aluminum seems to increase strongly with some content (about 1 to 4wt%), but with more aluminum content than 7 to 8wt% the sulfurization of alloys were much decreased.

Those characteristic behavior of the cast iron containing aluminum different from that of Fe-Al alloys is considered to have a close connection with the carbon content and its morphology in these alloys and also with that of corrosion product.

2. Morphology and Structure of Sulfide Scale

An example of the characteristic feature of scale after corrosion was indicated in Photo. 1. Some cracks are observed on the scale formed at the corner of all the test pieces containing aluminum as shown in these photographs. Moreover, there are two kinds of scale surfaces, one being a convex type of the surface (for

Photo. 1. Characteristic feature of sulfide scale after corrosion. Magnification: about 1.5 diameter

such as 201, 203, and 204 alloys), the other a concave one (for such as 207 to 225 alloys). All sectional views of those scales formed on the corroded alloys showed that the scale was consist of two layers (inner and outer ones), the outer one being very thin and showing brittle big grains, the inner one, on the contrary, occupying almost all scale thickness with much porosity and without any crystallinity under the macroscopic observation.

However, the alloy free from aluminum (200) has no crack and consists of the thicker outer layer and also the boundary of an outer/inner interface coincides with the original surface of the test piece as has been reported.⁴⁾ The direct observation of corrosion process indicated that the crack formation on the scale corner occurred during the growth of scale by corrosion but not on quenching the test piece after corrosion.

3. X-ray Analysis of Sulfide Scale

The result of the X-ray analysis of sulfide scale grown on each test piece during corrosion was indicated in Fig. 4. This analysis was mainly made of the inner scale of sulfide, because the outer scale was so thin that it could not be identified separately. However, from the external appearance it seemed to be composed mainly of FeS phase.

From the above analysis the scale was seemed to consist of pyrrhotite (corresponding to peaks of Nos. 2, 4, 5, 7, 8, and 10 in Fig. 4). In the scale of high aluminum alloys from 210 to 225, there were other diffraction patterns different from those of pyrrhotite (corresponding to peaks of Nos. 3, 1, 6, and 9), each of which showed the stronger value with increasing aluminum content. Among these peaks No. 3 was identified as that from Al_2S_3 in spite of somewhat uncertainty because of only one peak, and Nos. 1 and 6 peaks as well as No. 9 seemed to come from that of

Fig. 4. X-ray diffraction patterns from sulfide scale (mainly inner one) under the various conditions

* The number written after the alloy number indicates corrosion time (hr).

** This pattern shows that from outer scale of sulfide.

the double sulfide of iron and aluminum (FeAl_2S_4).^{5,7)}

This double sulfide was previously synthesized in our laboratory⁷⁾ and this crystal was identified as a hexagonal form having $a_0=3.639 \text{ \AA}$ and $c_0=36.16 \text{ \AA}$. On the contrary, Flahaut⁸⁾ also composed this compound (FeAl_2S_4) having parameters of $a_0=3.659 \text{ \AA}$ and $c_0=35.70 \text{ \AA}$. These two compounds may be identical. Anyhow, the new compound found in the inner scale of these alloys is supposed to be the same as that stated above.

Fe: 1×10^6 c.p.m.Al: 1×10^5 c.p.m.S: 1×10^6 c.p.m.

(a) EPMA patterns of Fe, Al, and S from 219 alloy at 900°C for 25 hr

Fe: 1×10^6 c.p.m.Al: 1×10^5 c.p.m.C: 3×10^4 c.p.m.

(b) EPMA patterns of Fe, Al, and C from 225 alloy at 900°C for 16 hr

Fig. 5. EPMA patterns of the components of test pieces under the various conditions

4. Change in Composition of the Alloy during Corrosion

The test piece was found to change in its composition of the components in the substrate after corrosion. One of the results, for example, was shown in Fig. 5. From this figure it was observed that the concentration of aluminum near the scale/alloy interface lowered. In the case of 219 alloy (a), the decomposition of the *K* phase which is an intermetallic compound having higher aluminum content occurred as stated later.

The soluble carbon in the alloy has a tendency to enrich in the substrate near the interface,⁹⁾ but the carbon as graphite or that in the *K* phase in the substrate does not move on its own. Thus it seems to be released into the sulfide scale during corrosion. Furthermore, it is notable that there is a preferential sulfur attack into the grainboundaries of the substrate.

5. The Marker Movement

In order to determine which atomic species is more

Marker (Pt wire: 0.5 mm ϕ)

Photo. 2. Position of Pt wire marker after corrosion of 204 alloy at 900°C for 1 hr

Magnification: 3.0 diameter ($\times 3/4$)

movable during the scale growth, fine platinum wire was wound up around the test piece before corrosion. At first, all fine platinum wires used as the marker ($40 \mu\phi$) were broken down from the scale surface during corrosion, so that a little thick wire (about $500 \mu\phi$) was used in the end. The result was shown in Photo. 2, in which it was notable that the scale strongly deformed near the platinum marker and that the marker wire was always on the outer/inner layer interface of the scale.

From the above observation it is concluded that the inward migration of sulfur atoms is predominant on the scaling of these alloys. However, sulfur assumes not to diffuse in through the scale as the lattice diffusion of sulfur ions, but to migrate through cracks or voids of the scale in a gaseous state as will be discussed later.

IV. Discussion of Results

It has been generally recognized that the corrosion of iron and steel in sulfur vapor obeys a parabolic rate law if the scale formed on those metals is dense, and iron atoms are more predominantly movable species than sulfur atoms.¹⁰⁾ However, there are many examples that the difference of alloying element in the iron substrate changes markedly the morphology of scale resulting in the change of its growth rate.⁵⁾ In general, the sulfur attack against an alloy produces two layers at least, one being a dense outer layer and another a porous inner layer.⁹⁾ The latter layer is formed even in the case of the corrosion of pure metal in sulfur vapor. The schematic illustration of the behavior of two scale layers and the corresponding marker position were shown in Figs. 6 (a) to (d) from the observations performed hitherto in our laboratory, where the shaded parts were inner layers and the chain lines shown in Figs. 6 (a) and (b) were considered to be the position of the original surface of test pieces, and especially, the common cast iron (here, corresponding

Fig. 6. Schematic illustration of the marker position as well as the morphology of sulfide scale on different alloys

to No. 200 alloy) showed the original surface of a test piece coinciding with the outer/inner interface as shown in Fig. 6 (c). On the contrary, the present results corresponded to Fig. 6 (d), in which the marker seemed as if it would lie on the surface of the scale because of the very thin outer layer.

Accordingly, as for those observations obtained from above Figs. 6 (a) to (c), the mechanism of the formation of an inner layer is considered as follows, when such a thick and dense outer layer is formed that sulfur can not penetrate into the inner part of scale in the gaseous state:

The accumulation of vacancies at a metal/scale interface produces many voids at that place when cations diffuse out through the sulfide scale. Moreover, the plastic flow of the scale will be disturbed by the so-called "corner effect." Then, in order to fill up the cracks or voids near the metal/sulfide interface, the sulfur vapor supplied by the decomposition of the sulfide near the defects reacts with the substrate to produce the new sulfide on the surface of the substrate. From such a consideration the inner layer is assumed to be a secondary product as Wagner verified by means of a pellet method.¹¹⁾

However, there are still many ambiguous points in the formation of an inner layer during sulfurization. In this case there is found to be the so-called "composite scale" owing to the high enrichment of other sulfides and/or graphite flakes than pyrrhotite coming from alloying elements. Therefore, the inner layer can be considered to play an important role in the process of scale growth, as Mrowec *et al.*¹²⁾ suggested in their study.

In this experiment almost all test pieces had the scale of which the inner layer occupied a greater part of the total scale thickness and also had no scale at the corner of the substrate. These phenomena are better considered as follows:

The test pieces of 201 to 204 alloys will release off the graphite particles in the substrate into the inner sulfide scale during corrosion and thus the scale consists of pyrrhotite and graphite. This inner scale will disturb the plastic deformation of the total scale and moreover, the contact between pyrrhotite and graphite will be loose, so that some cracks and/or voids in the scale will be produced and make paths for sulfur vapor. Therefore, the corrosion reaction will proceed at the scale/alloy interface, and then the reaction will obey a linear rate law and the corrosion rate will be much greater. In the case of test pieces of 207 to 225 alloys carbon is involved mainly in K phase ($\text{Fe}_3\text{AlC}_{0.66}$),⁶⁾ so that during corrosion the K phase will decompose at the scale/alloy interface and carbon will be dispersed into the scale as finer graphite particles. The scale morphology on each alloy is as shown in Photo. 1.

The increase of corrosion resistance against sulfur attack shown in the case of alloys with higher aluminum content will be due to the formation of Al_2S_3 and FeAl_2S_4 in the inner scale as determined by means of the X-ray analysis as well as the scale morphology stated above. These compounds decrease the migration paths of sulfur, the corrosion rate looking like obeying a parabolic rate law.

As has been reported of corrosion test of commercial cast iron used for sulfur smelting pot by the same author,⁴⁾ aluminum-containing cast iron (3.34wt% C, 3.62wt% Al, 1.79wt% Si, and 0.40wt% Mn) did not show any cracking at the corners of scale grown on the test piece at 900°C up to 10 hr. This different behavior even in aluminum-cast iron will be notably due to the other constituents such as silicon and manganese contained in the cast iron. Accordingly, it is very interesting to note that the morphology of the scale formed on the test piece could be changed even in the small quantity of these additional elements. In this case, therefore, the minor elements contained in the alloy would give the significant different effect on the scale at the beginning of corrosion, because depending upon the morphology or the compactness of the scale at the early stage of corrosion the subsequent form of the scale will be in general much influenced, whether the outer layer may be thick or not, and whether the newly formed special compounds may be lamellar or dispersive.

A fairly similar feature of the scale growth to that found in this experiment was recently reported by Bruns¹³⁾ in the corrosion of an Fe-14.8wt% Al-2.98 wt% Mo alloy in H_2S atmosphere, but the reason or mechanism of this unusual phenomenon was not mentioned. Furthermore, many years ago Scheil¹⁴⁾ and other workers¹⁵⁾ also showed the same behavior in the oxidation of alloys containing WC and TiC and thus they suggested that CO or CO_2 gas was produced in the scale, where some voids were formed, and through

(a) Cross section view of corroded platinum ($\times 200$) ($\times 2/3$)

(b) Magnified view of (a) showing alumina marker ($\times 780$) ($\times 2/3$)

Photo. 3. Characteristic feature of sulfide scale on platinum wire (100 micron in diameter) after corrosion for two weeks at 680°C under an atmospheric pressure of sulfur vapor

the voids in the scale O_2 gas was movable more easily.

On the contrary, the present authors have found the similar sulfide scale formation on the platinum metal wire during sulfur attack.¹⁶⁾ For example, Photo. 3 and Fig. 7 show the case. This behavior will be probably due to the property of the sulfide scale grown on the metal that sulfur atoms will be able to pass dominantly through the scale. Even in some metallic alloys^{17,18)} it is accepted that such a diffusion similar to these phenomena can occur.

Accordingly, the inward migration of an ambient sulfur component alone and also the formation of the porous aluminum sulfides having a greater molar volume than that of iron sulfide will be necessary for the successive construction of the sulfide scale with its re-entrant edges, and thus it is concluded that such a morphology will be the very strong evidence that an ambient component diffuses in or migrates through the newly formed phase.

V. Summary

Fe-2wt% C-Al (up to 25wt%) alloys were corroded under the atmospheric pressure of sulfur vapor at 900°C and the following results were obtained:

(1) The addition of small amount of aluminum to an Fe-2wt% C alloy increased the corrosion rate very much, showing the behavior similar to the reaction control.

Fig. 7. EPMA patterns of platinum and sulfur from the sulfurized platinum wire for two weeks at 680°C
Pt: 3×10^5 c.p.m., S: 1×10^6 c.p.m.

(2) On the contrary, the addition of aluminum more than 7 to 8wt% increased markedly the corrosion resistance of the alloy. From the result of X-ray diffraction patterns the special compounds such as Al_2S_3 and FeAl_2S_4 were determined to be contained mainly in the inner scale, and these compounds were deduced to contribute the prevention of corrosion in sulfur vapor.

(3) Kinetically at the early stage of corrosion alloys with higher aluminum content showed the diffusion controlling behavior, but afterwards it showed the sudden increase of corrosion, that is, the so-called "break-away."

(4) After corrosion almost all alloys showed the scale morphology without corners except 200 alloy, and the scale consists of two layers, of which the inner layer was the greater part of the scale, and very porous and brittle.

(5) Platinum marker was always found on the outer/inner scale interface, so that the inward migration of sulfur atoms seemed to be predominant. This phenomena will have some connection with the carbon released into the sulfide scale from the alloy matrix during corrosion, thus the reason of the characteristic behavior of the marker will be due to the formation of cracks and/or voids to be paths for sulfur gas in the scale.

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