Anodic Polarization Behavior of Iron-Silicon Alloys*

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Seven iron-silicon alloys having various silicon contents up to about 14% were polarized in 2 N H₂SO₄. The relationship between silicon contents in the alloys and various properties such as the maximum or the limiting current density and the passive potential and the passive current density were investigated. 14% silicon alloy is much easier to passivate than iron, because the maximum current density of the 14% alloy is equivalent to one-hundredth as large as that of iron and the passivation potential of the 14% alloy is close to its corrosion potential. An unusual variation in the passive current density with silicon content was observed; the passive current density increased with increasing Si content up to 6%, but decreased with increasing Si content above 6%.

The anodic polarization measurements were also carried out in 1 and 0.5 N H₂SO₄ with three iron specimens, 6 and 14% Si. The polarization behavior of the 6% alloy was only affected by the sulphuric acid concentration. In 1 and 0.5 N H₂SO₄, the transition region from the active to passive state of the 6% alloy extended to the noble potential side accompanying a violent current oscillation. Such passivation phenomena can be explained to some extent on the basis of the silica formation on the anode surface.

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I. Introduction

Iron-silicon alloys containing about 14% silicon have excellent resistance to both oxidizing and non-oxidizing acids. For this reason, high silicon cast iron has been practically used as a corrosion resistant material to acids.

In order to make clear the corrosion mechanism of the alloy in acids, the anodic polarization behavior should be investigated at first. Although several authors ascribed the excellent corrosion resistance of the iron-silicon alloys to the protective effect of the silica film⁽¹⁾⁽²⁾, little has been known about the anodic behavior of the alloys which has been reported.

The purpose of this study is to investigate the anodic behavior of the iron-silicon alloys containing silicon less than about 14% in a dilute sulphuric acid solution in relation to passivation behavior of the alloys. The role of silica film in the anodic behavior was also discussed.

II. Experimental Procedure

Seven iron-silicon alloys containing various silicon contents up to about 14% were prepared by means of silicon impregnation (so-called siliconizing) and subsequent diffusion annealing as reported in a previous paper⁽³⁾.

Commercial electrolytic iron was melted in vacuum with a high frequency furnace and casted to a 2 kg ingot. The ingot was forged and rolled to a sheet 1.5 mm in thickness. The iron sheet was cut out to disks with diameter of 24 mm. The iron disks were employed for the siliconizing and subsequent diffusion annealing.

The apparatus for the siliconizing treatment is shown in Fig. 1. Oxygen-free argon containing 10 vol% silicon tetra-chloride was passed through the reaction pipe at a flow rate of 30 mL/min.

Table 1 shows the conditions for the preparation of the iron-silicon alloys. In the columns of the siliconizing time

Fig. 1 Siliconizing apparatus

① Argon gas	⑥ Flow meter
② KOH	⑦ SiCl ₄
③ Active copper	⑧ Reaction tube
④ Silica gel	⑨ Specimen
⑤ P ₂ O ₅	

Table 1 Conditions for preparation of the iron-silicon alloys containing various silicon contents

Specimen	Siliconizing		Heating		Silicon content (%)	
	Temp. (°C)	Time (min)	Temp. (°C)	Time (hr)		
iron	—	—	1235	0.5	0.0	
3% Si	1235	15 × 2	1235	20	Dif- fusion	2.9
6% Si	1235	30 × 2	1235	20		6.3
9% Si	1235	30 × 3	1235	20 × 2		9.3
11% Si	1235	30 + 40	1350	1	Melting	10.6
13% Si	1235	30 + 45	1350	1		13.0
14% Si	1235	30	—	—		14.4

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and the diffusion annealing time, the number which follows a cross sign denotes the number of the treatments. For the preparation of the 6% silicon alloy, for example, one side of the iron disk was siliconized for 30 min, and then the other side, for 30 min. After removing the circumferential edge of the siliconized disk by grinding, the diffusion annealing was carried out in argon atmosphere for homogenization. In order to prepare the 9% silicon alloy, the 6% silicon alloy was siliconized for 30 min again. By repeating the cutting and the diffusion annealing, a 9% silicon alloy was obtained.

A different method was used to prepare the iron-silicon alloys containing more than 10% silicon, because it was considerably time consuming to obtain a high silicon alloy by the above method. For the preparation of the 11 and 13% silicon alloys, each side of the iron disk was siliconized for the times shown on both sides of the plus sign in Table 1, and then the siliconized disk was kept for 1 hr at a temperature near the melting point. In this case, the alloy specimens obtained were button-shaped.

When the iron disk was siliconized for 30 min at 1230°C the disk was coated with a 0.3 mm thick ferro-silicon film with nearly constant 14.4% silicon. The specimen thus obtained, was employed as the 14% silicon alloy.

Pure silicon (polycrystalline, 99.9999%), fayalite Fe_2SiO_4 and a sintered iron-silica powder compact were used in this experiment.

Fayalite: Höganäs iron, hematite Fe_2O_3 and silica SiO_2 powder were mixed to form the stoichiometric composition of Fe_2SiO_4 . The mixture was cold pressed at 3 t/cm² and fused in the flow of argon gas at 1250°C.

Sintered iron-silica powder compact: a known mixture of Höganäs iron and silica powder was cold pressed at 3 t/cm² and sintered in the flow of argon gas at 1050°C for 2 hr. The sintered compact was pickled in molten paraffin wax to avoid the penetration of sulphuric acid solution.

All the specimens were abraded with 0/3 emery paper, degreased with acetone and then coated with Dekhotinsky cement, allowing an area of 0.25 cm² to be exposed to sulphuric acid solution.

Dilute sulphuric acid solution was prepared from a pure reagent and distilled water. Nitrogen gas, purified by a successive passage through the active copper tower and an acid chromus chloride solution, was bubbled vigorously into the solution for 2 hr to deaerate the solution. Fig. 2 shows the polarization cell used. The solution was thermostatically controlled at $25 \pm 0.1^\circ\text{C}$.

All polarization measurements were conducted using a potentiostat with the capacity of 100 mA and the response of 10^{-1} sec. A saturated calomel electrode and a 1N H_2SO_4 mercurous sulphate electrode were used as the reference electrodes. After immersion for 20 min, the corrosion potential was determined and then polarization measurements were carried out. In case of necessity, cathodic polarization with a constant current density of 10 mA/cm² was conducted for ten min in order to obtain the oxide-free surface. After completion of the cathodic polarization, the polarization to a noble side started from the potential required to give the current density mentioned above. While increasing the potential at intervals of

20 mV, the current was determined after the lapse of one min at each increment. In the present paper the potential was represented by the standard hydrogen scale and the current density was calculated on the basis of the geometric area of the specimen.

Fig. 2 Polarization cell

① To the reference electrode	④ Sintered glass
② Anode specimen	⑤ Platinum auxiliary electrode
③ Nitrogen gas inlet	⑥ Nitrogen gas outlet

III. Results and Discussion

1. Anodic behavior of iron-silicon alloys in 2N H_2SO_4

No notable relationship between the corrosion potential and the silicon content was observed as shown in Fig. 3. Fig. 4 shows the anodic polarization curves for seven iron-silicon alloys. Each polarization curve for the iron specimen and for the 3 and 6% silicon alloys has two current peaks and a violent oscillation region of the current which appears just after the second peak. The alloys containing 9 and 10% silicon passivate without the current oscillation, although these alloys also have two current peaks respectively. In each polarization curve for the 13 and 14% silicon alloys there is only one peak having a very low current value. All of the electrodes in the passive state begin to evolve oxygen gas at the potentials between 1.75 and 2.0 V. Further polarization above the oxygen evolution potential, however, does not give rise to the

Fig. 3 Corrosion potential vs. silicon content

Fig. 4 Anodic polarization curves for seven iron-silicon alloys in $2\text{Na}_2\text{SO}_4$. (1) iron (2) 3% Si (3) 6% Si (4) 9% Si (5) 11% Si (6) 13% Si (7) 14% Si

transpassive state as seen in the iron-chromium system⁽⁴⁾ and the iron-nickel⁽⁶⁾ system.

When two current peaks appeared, the current density at the second peak was chosen as the maximum current density. Variations in the maximum current density and in the potential corresponding to the maximum current density with silicon content are shown in the upper and lower parts of Fig. 5, respectively. Both of the maximum current density and the corresponding potential are nearly constant in the composition range of 0 to 6% silicon, beyond which, the values decrease with increasing Si content. For the 14% silicon alloy the maximum current density is about one-hundredth of that for the iron specimen.

Fig. 5 The maximum current density and the corresponding potential vs. silicon content

men and the corresponding potential approaches the corrosion potential.

The maximum current density and the corresponding potential were often defined as the passivation⁽⁴⁾ or the limiting⁽⁷⁾⁽⁸⁾ current density and the passivation potential⁽⁴⁾⁽⁸⁾, respectively. The decrement of the passivation current and the approach of the passivation potential to the corrosion potential give rise to easy passivation. It can be thought, that the 14% silicon alloy passivates much easier than the iron specimen. This should be one of the reasons that the 14% silicon alloy has excellent resistance to corrosion.

The passive current density, which is regarded as the maximum current density required to maintain passivity, was evaluated at 1.25 V corresponding to the middle potential in the passive region. As shown in Fig. 6, the passive current density increases with increasing silicon content up to 6%. For the alloys containing more than 6% silicon, the passive current density decreases with increasing silicon content and becomes less than that for iron at more than 13% silicon. The passive current density for the 6% silicon alloy is equivalent to about one hundred times greater than that for the iron specimen. This phenomenon suggests that the passive state of the 6% silicon alloy is extremely unstable.

Fig. 6 The passive current density vs. silicon content

Observation of the exposed anode surfaces during the polarization measurements indicated that the anodes except for the 6% silicon alloy had almost the same appearance as that just after the immersion. When the 6% silicon alloy was polarized at the potential nobler than 0 V corresponding to the first peak, this anode surface was surrounded by a white corrosion product which successively moved into the solution by the violent anodic dissolution of the alloy.

2. Anodic behavior of iron-silicon alloys in 1 and 0.5N H_2SO_4

The iron specimens and the 6 and 14% silicon alloys were polarized in 1 and 0.5N H_2SO_4 . The anodic behavior of the 6% silicon alloy is only affected by the sulphuric acid concentration. In 1 and 0.5 N H_2SO_4 , the region of the current oscillation for the polarization curve of the 6% silicon alloy is extremely extended to the nobler side as shown in Fig. 7. Since the increase of pH has an effect of shifting the entire polarization curve to a more active side, the increase of pH by the dilution must be irrelevant to the extension. For the purpose of examining the effect of the sulphate ion concentration on the anodic

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behavior of the 6% silicon alloy, the polarization measurement was conducted in a solution which was adjusted to have the same sulphate ion concentration as that in 2N H_2SO_4 by the addition of Na_2SO_4 to 1N H_2SO_4 . The result is shown in Fig. 8 in comparison with the polarization curves for 1 and 2N H_2SO_4 . In each polarization curve for 2N H_2SO_4 and for $\text{Na}_2\text{SO}_4 + 1\text{N } \text{H}_2\text{SO}_4$, the current oscillation ceases at 0.56 V.

Fig. 7 Anodic polarization curves for the 6% silicon alloy in 2, 1 and 0.5N H_2SO_4

Fig. 8 Anodic polarization curves for the 6% silicon alloy in 2 and 1N H_2SO_4 , and in 0.5, 1N $\text{H}_2\text{SO}_4 + \text{Na}_2\text{SO}_4$

Morioka and Sakiyama⁽⁹⁾ observed that the passivation potential of iron in 0.4N H_2SO_4 shifted to a more noble side than that in 2N H_2SO_4 . One of them investigated this phenomenon as a function of sulphate ion concentration in detail, and reported that the sulphate ion facilitated the anodic passivation of iron⁽¹⁰⁾. From these results and the fact that the passivation of the 6% silicon alloy delays even in 1N H_2SO_4 , it may be considered that the

6% silicon alloy is more difficult to passivate than iron.

The exposed surface of the 6% silicon alloy during the polarization measurement in 1N H_2SO_4 was surrounded by the white corrosion product in the same manner as mentioned previously. The amount of the product gathered from the solution after the polarization measurement was too small to be analyzed. To obtain a sufficient amount of the product for X-ray analysis, the 6% silicon alloy was kept at the potential of 0 V for 50 hr. 0.1 g of the product thus obtained was washed with water, dried in a desiccator at room temperature, and then subjected to X-ray analysis. As shown in Fig. 9, the diffraction pattern indicates that the product is quartz, but it should be called silica because the product in the solution might exist in the form of a hydrate.

Fig. 9 X-ray diffraction pattern of the white product ($\text{CoK}\alpha$, Fe filter)

3. Anodic behavior of pure silicon and fayalite electrodes in 1N H_2SO_4

The polarization curves for pure silicon and fayalite electrodes in 1N H_2SO_4 are shown in Fig. 10 in comparison with the curves for the iron specimen, and the alloys containing 6 and 14% silicon. Polarity of four electrodes except for fayalite changed at -0.25 V, because these electrodes were polarized from the cathodic to the anodic region after the cathodic cleaning. The anodic current for the pure silicon reaches the saturating value at -0.2 V. At this potential, the curves for the 6 and 14% silicon alloys begin to deviate in the noble direction from the curve for the iron electrode.

According to a potential-pH diagram of silicon⁽¹¹⁾, silicon is a powerful reduction agent. It decomposes water with the evolution of hydrogen and gaseous silicon hydride SiH_4 , and forms silica and silicate at a more active potential than the potential investigated here. In most cases, however, the high reactivity of silicon does not often appear at room temperature. This is probably because of the remarkable irreversibility of the oxidation reduction reaction of silicon and passivation of silicon by the formation of a silica film⁽¹¹⁾. If the potential and the process of the silica formation are not strictly considered, it is reasonable to consider that the pure silicon electrode was passivated by the formation of a silica film at -0.2 V in Fig. 10. The deviation of the curves for the 6 and 14% silicon alloys from that for the iron specimen at -0.2 V should be due to the silica formation in the same manner as in case of the pure silicon electrode.

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Fig. 10 Polarization curves for the iron, the 6 and 14% silicon alloys, the pure silicon and the fayalite in $1N H_2SO_4$

Nakajima and Maekawa⁽¹²⁾ reported that the first current peak in the anodic polarization curve for iron is caused by wüstite formation. If wüstite is formed on the surface of the iron-silicon alloy electrodes, fayalite might be produced by the reaction of wüstite with silica. However, as shown in Fig. 10, it is not valid to consider that fayalite governs the anodic behavior of iron-silicon alloys, because the behavior of fayalite is not similar to that of the iron-silicon alloys.

4. Effect of the holding of a constant potential on the anodic behavior of iron-silicon alloys

In order to obtain further information on the silica formation, the 6 and 14% silicon alloys were polarized in $1N H_2SO_4$ again, and then held for 1 hr at $-0.2 V$ corresponding to the potential at which the polarization curves for the alloys began to deviate from the curve of the iron specimen. The behavior of the 6% silicon alloy was not affected by the holding of the constant potential, but for the 14% silicon alloy the anodic current density at $-0.2 V$ markedly decreased by the holding and the current density in the active region nobler than $-0.2 V$ decreased as shown in Fig. 11. These results show that the silica formed on the exposed surface of the 6% silicon alloy is successively released into the solution without its accumulation on the surface. On the contrary, for the 14% silicon alloy, it is reasonable to consider that the silica is accumulated during the holding intervals, resulting in the marked decrease of the current.

Fig. 11 Effect of the maintenance at $-0.2 V$ on the anodic polarization curve for the 14% silicon alloy in $1N H_2SO_4$

5. Flade potential of the iron-silicon alloys

For obtaining the Flade potential of the iron specimen and the 6 and 14% silicon alloys, the current was cut off after each electrode was held for 1 hr at $1.4 V$, and then the potential decay was traced by an automatic recorder. The arrest of the potential decay curve for the 6% silicon alloy was difficult to record because of the very brief decay of potential. Both of the decay curves for the iron specimen and the 14% silicon alloy arrested at $0.55 V$ as shown in Fig. 12. Since the pH of $1N H_2SO_4$ is about 0.6, the above arrest potential agrees with the Flade potential which is represented by Frank's equation of $E_F = 0.56 - 0.059 pH$ ⁽¹³⁾.

Fig. 12 Potential decay curves for the iron, the 6 and 14% silicon alloys in $1N H_2SO_4$

Because the Flade potential is the equilibrium activation potential of a passive metal, it should be identified with the equilibrium potential for the initiation of the passive film formation. The agreement of the Flade potential for the 14% silicon alloy with that for iron suggests that the composition of the passive film for the 14% silicon alloy is essentially the same as that for iron. It can be

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understood, therefore, that the passivation of the 14% silicon alloy is completed by the filling up the gaps of the silica layer previously formed in the active state with the passive film of iron.

6. Anodic behavior of the sintered iron-silica powder compact

Fig. 13 shows the anodic curve for the sintered compact in a mixing ratio of 8 parts Fe to 1 part SiO_2 which corresponds to the composition of 6% silicon. The anodic behavior of the sintered compact indicates the same trend as that of the 6% silicon alloy; the passivation of the sintered compact in 1N H_2SO_4 becomes difficult as a result of the extension of the current oscillation region to the noble side. As a matter of course, it cannot be considered that both surfaces of the sintered compact and of the 6% silicon alloy are in the same condition. In each case, however, a fresh surface abruptly appears when silica departs from the surface under the successive anodic dissolution of the electrode. The current oscillation prior to the passivation indicates that the anode is in the transition range from the active to the passive state. Because the anode in the transition range is especially sensitive to the external and internal disturbances, the abrupt appearance of the fresh surface would cause the extension of the current oscillation region.

Fig. 13 Anodic polarization curves for the sintered iron-silica compact (8 Fe-1 SiO_2) in 1 and 2 N H_2SO_4

7. Immersion tests in concentrated nitric acids

All of the specimens were abraded with 0/3 emery paper, degreased with acetone and then coated with Ful-lontex, allowing only an area of 1 cm^2 to be exposed to nitric acid (60~62% HNO_3). Table 2 shows weight loss of the specimen after immersion for 30 min at 25°C .

Corrosion loss of the 6% silicon alloy and the sintered compact is by far larger than that of the other specimens, and the 14% silicon alloy and pure silicon show a minimum corrosion loss. This trend is similar to the behavior of the passive current density shown in Fig. 6.

Table 2 Corrosion loss of the specimens in concentrated HNO_3 (25°C , 30 min)

Specimen	Corrosion loss (mg/cm ²)
iron	53
6% Si alloy	148
14% Si alloy	23
pure silicon	23
8 Fe-1 SiO_2 sintered compact	108

IV. Summary

(1) Anodic polarization behavior of seven iron-silicon alloys containing less than about 14% silicon was investigated in 2N H_2SO_4 . For the alloy with less than 6% silicon, both of the maximum current density and the potential corresponding to the maximum current density are constant independent of silicon content. For the composition of more than 6% silicon, however, the maximum current density increases with increasing silicon content and the corresponding potential approaches the active direction. For the 14% silicon alloy, the maximum current density is very low and the corresponding potential is very close to the corrosion potential. Therefore, the 14% silicon alloy becomes easily passive. This may be a cause impart the 14% silicon alloy the excellent resistance to corrosion. The effect of the silicon content on the passive current density is quite different from the tendency mentioned above; the passive current density increases with increasing silicon content up to 6%, but decreases with increasing silicon content above 6%.

(2) The anodic polarization measurements of the iron specimen and the 6 and 14% silicon alloys were carried out in 1 and 0.5N H_2SO_4 . The polarization behavior of the 6% silicon alloy is only affected by the sulphuric acid concentration. For the 6% silicon alloy in 1 and 0.5N H_2SO_4 the transition region from the active to passive state which accompanies a violent current oscillation extends to the noble potential side. This means that the 6% silicon alloy is difficult to passivate compared with iron. The successive departure of silica from the electrode surface in the transition state would cause the phenomenon mentioned above.

(3) From flade potential measurements it has been known that the composition of the passive film of the 14% silicon alloy is essentially the same as that of the iron specimen. It is reasonable to consider that the passivation of the 14% silicon alloy is completed by filling up the gaps of the silica film previously formed in the active state with the passive substance of iron.