Effect of Titanium Addition on Carbon Deposition on Iron in Carburizing Gas

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The behavior of carbon deposition on as-polished or pre-oxidized Fe-Ti alloys containing 0–2.11 mass% Ti in a 10%CH₄–H₂ mixture at 1203 K was studied by metallography and thermogravimetry. Titanium retarded carburization and carbon deposition by changing the microstructure of the alloys from austenite to ferrite in which the solubility limit of graphite is much lower and by forming a stabler carbide (TiC) than Fe₃C. In particular, carbon deposition on as-polished alloys containing 0.67 mass% Ti or more was markedly depressed because of the formation of TiO₂ on the surface despite the carburizing atmosphere. Under this condition, TiO₂ may have formed by the reaction of titanium in the alloys with small amounts of oxidizing gases such as O₂ and H₂O present in the atmosphere. On oxidation in air, Fe₂O₃, Fe₃O₄, and FeO formed on iron and a small addition of titanium (0.09 mass% Ti) retarded the formation of FeO and a further addition of titanium up to 2.11 mass% caused the formation of FeO·TiO₂ and TiO₂ besides Fe₂O₃ and Fe₃O₄. The exposure of the alloys containing 0.67 mass% Ti or less to the 10%CH₄–H₂ mixture after the oxidation in air led to a sudden mass loss in the early stage and then a rapid mass gain. This mass change is primarily ascribed to mass loss by reduction of iron oxides and to mass gain by carbon deposition. The rapid mass gain by carbon deposition is probably due to the formation of active iron by reduction of iron oxides and to the increase in the reaction area by spallation of the scale; the active iron formed may promote the direct deposition of filmy carbon on the surface and filamentous carbon deposition through Fe₃C formation and decomposition. Carbon deposition on the alloys containing 1.40 mass% Ti or more, however, was considerably depressed because TiO₂ formed during the oxidation remained even during carburization, although the amounts of carbon deposition increased compared with those on the as-polished alloys owing to the coexistence of reducible iron oxides.

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I. Introduction

In the processes which utilize the pyrolysis reaction of CO or hydrocarbons, carbon deposition, generally called sooting or coking, occurs and causes various troubles in operation such as loss of control of the carbon potential and deterioration of furnace alloy and refractory⁽¹⁾⁽²⁾. Hence, it is important to minimize carbon deposition and carburization for the heat-resisting steels used under these carbon depositing atmospheres.

We have studied the effects of alloying elements (chromium⁽³⁾⁽⁴⁾, silicon⁽³⁾, nickel⁽⁴⁾ and

aluminum⁽⁵⁾⁽⁶⁾) on carbon deposition on iron alloys in CO–H₂ or CH₄–H₂ gas mixtures for a better understanding of the behavior of carbon deposition on high temperature steels with high contents of these alloying elements in carbonaceous atmospheres and found the following facts: chromium and nickel retard carbon deposition by the formation of stable protective carbides, and by the reduction of catalytic effect, respectively, whereas silicon and aluminum promote filamentous carbon deposition because of the acceleration of decomposition of Fe₃C formed on the surface. In addition, chromium oxides or alumina which was observed to form on high chromium steels or high aluminum alloys even in carburizing atmosphere were found to retard carbon deposition^{(4)–(7)}. From these results, for instance, the formation of stable noncatalytic compounds such as carbides and oxides on steels can be

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considered as one of the methods for retarding or preventing carbon deposition.

Titanium is usually added under 1 mass% with chromium to heat-resisting steels for the purpose of improvement of oxidation resistance⁽⁸⁾. It is a carbide forming element and has a strong affinity for oxygen like chromium⁽⁹⁾. Thus, titanium is expected to have a favorable effect on the retardation or the prevention of carbon deposition. However, the influences of titanium and its oxide on carbon deposition in carburizing atmospheres have not yet been clarified.

The aim of the present work is to investigate the behavior of carbon deposition on as-polished or pre-oxidized iron-titanium alloys containing 0–2.11 mass% Ti in carburizing gas at 1203 K which is a usual carburizing temperature to elucidate the effects of titanium and its oxide on carbon deposition on the alloys.

II. Experimental Procedures

The chemical composition of the iron-titanium alloys used in this study are given in Table 1. Since addition of titanium of more than about 2.5 mass% to iron may form Fe₂Ti from the phase diagram for the Fe–Ti system⁽¹⁰⁾, it was limited to 2.11 mass% in the present experiment. These alloys were vacuum-induction melted using an electrolytic iron (>99.95 mass% Fe) and a ferrotitanium (Fe–44.0 mass% Ti alloy). The alloy ingots were forged and then homogenized at 1273 K for about 54 ks (15 h). After surface finishing, this material was sectioned into a coupon of 1 × 20 × 40 mm³. The surfaces of the specimens were mechanically polished with emery paper up to 600 grit. All the specimens were cleaned ultrasonically in acetone prior to the experiments.

The variation of mass gain occurred by carburization and carbon deposition with time was measured with an apparatus which consisted of a gas purifier, a heating furnace and a thermobalance. The gas purifier was installed to remove impure gases present in CH₄ and H₂. Gas analyses were performed by gas chromatography. A kanthal wire-wound resistance furnace was used, and the temperature was automatically controlled within approximately ±1 K. The hot zone was about 80 mm long with a temperature variation of ±3 K. The reaction tube was a non-transparent quartz tube 1 m in length and 28 mm in inner diameter. The thermobalance consisted of an automatic balance with a capacity of 100 g and a sensitivity of 0.1 mg and a recorder by which the mass gain of the specimen hung with quartz fibers was continuously recorded. The specimen was first heated in pure H₂ gas for about 1.8 ks (30 min) at 1203 K. Then the carburization experiments were carried out at the gas velocity of $4.06 \times 10^{-2} \text{ ms}^{-1}$ in the 10%CH₄–H₂ mixture.

The oxidation experiments were conducted in air at 1203 K which was introduced from the bottom of reaction tube. In this case, the atmosphere was quickly replaced from pure H₂ through Ar to air after preheating the specimens. The specimen after the oxidation in air was successively exposed to carbonaceous atmosphere by replacing air through Ar to the 10%CH₄–H₂ mixture. Mass change during these reactions was continuously measured in the same way as described above. The surface condition of each specimen after the reaction was observed with a scanning electron microscope and the deposits on the surface were identified by X-ray diffraction.

III. Results and Discussion

1. Carbon deposition on as-polished alloys

Figure 1 shows the mass gain curves of iron-titanium alloys measured with the thermobalance. It can be seen from this figure that mass gain obviously decreases by small addition of titanium. Incidentally, titanium is known to decrease the diffusivity of carbon in

Table 1 Chemical composition of specimens (mass%).

Specimen	C	Si	Mn	P	S	Ti
Iron	0.002	<0.005	<0.01	<0.003	0.006	—
Fe–0.09Ti	0.002	0.006	<0.01	<0.003	0.006	0.085
Fe–0.67Ti	0.002	0.013	<0.01	<0.003	0.007	0.670
Fe–1.40Ti	0.002	0.019	0.02	<0.003	0.007	1.395
Fe–2.11Ti	0.003	0.030	0.03	<0.003	0.008	2.113

Fig. 1 Effect of titanium on the rates of mass gain occurred by carburization and carbon deposition in 10%CH₄-H₂ mixture at 1203 K.

austenite⁽¹¹⁾. Also, according to the equilibrium diagram for the Fe-Ti system⁽¹⁰⁾, at 1203 K, the microstructure of Fe-0.09 mass% Ti alloy is austenite but that of the alloys containing 0.67 mass% or more is ferrite in which solubility limit of graphite is much lower, indicating that mass gain by carburization can be neglected in the latter alloys. Thus, the depression of carburization by addition of titanium may have led to the decrease in mass gain of the alloys in Fig. 1.

Surface morphology of each specimen after the reaction is shown in Fig. 2. In iron, as depicted in Fig. 2(a) and (b), two types of carbon, filmy carbon and filamentous carbon are observed to deposit. We have already reported the mechanism for the deposition of these two types of carbon in the previous paper⁽¹²⁾⁽¹³⁾; filmy carbon nucleates and grows directly on the iron surface through the decomposition of carburizing gas at the active sites such as grain boundaries and dislocations, whereas the nucleation and growth of filamentous carbon proceed by the repetition of formation and decomposition of Fe₃C with the pyrolysis of carburizing gas on the substrate exposed by local break of filmy carbon. Morphologies of carbon deposits on iron-titanium alloys, however, are obviously different from that on iron as shown in Fig. 2(c) through (f). It is noted that filmy carbon is not observed and

only filamentous carbon deposits and that the amounts of filamentous carbon deposited on these alloys decrease markedly with increasing titanium content.

Typical X-ray diffraction patterns of the surface of the specimens after the reaction are illustrated in Fig. 3. Figure 3 shows that TiO₂ (brookite) and/or TiC as well as carbon and Fe₃C form on the alloys containing 0.67 mass% Ti or more. Therefore, the significant decrease in mass gain of the high titanium alloys as seen in Fig. 1 may be primarily ascribed to the retardation of carburization and carbon deposition by the formation of these compounds.

According to the studies on the graphitization of Fe₃C⁽¹⁴⁾, titanium is usually known as a nongraphitizer because of the formation of a stable carbide TiC. It is also considered that titanium does not solve in Fe₃C and hence has no direct effect on its stability⁽¹⁵⁾. On Fe-0.09 and -0.67 mass% Ti alloys, TiC are not identified by X-ray diffraction as shown in Fig. 3(b) and (c). However, considering that the deposition of filamentous carbon on the alloys is evidently retarded compared with that on iron as depicted in Fig. 2 and that TiC can form on the surfaces from the phase diagram for the Fe-Ti-C system⁽¹⁶⁾, a small amount of TiC which is undetectable by X-ray diffraction may retard carbon deposition.

Brookite formed on the high titanium alloys and rutile are allotropes of TiO₂⁽¹⁷⁾. As will be described later, rutile forms on them during the oxidation in air. Since further information on these allotropes was not available, the reason why brookite or rutile formed in carburizing gas or in air, respectively, could not be clarified. This formation of an oxide in the carburizing atmosphere was also observed in the previous experiments on carbon deposition on Fe-Al alloys⁽⁵⁾⁽⁶⁾. The formation of TiO₂ in carburizing gas, as reported previously about the formation of Al₂O₃⁽⁵⁾, is probably due to the reaction of titanium in the alloys with small amounts of oxidizing impure gases such as O₂ and H₂O present in the atmosphere. Incidentally, the partial pressure of oxygen, P_{O_2} , in the present atmosphere was calculated from the measurement of dew point in exhaust gas

Fig. 2 Scanning electron micrographs of carbon deposited on the specimens in 10%CH₄-H₂ mixture at 1203 K. (a) and (b) iron, (c) Fe-0.09 mass% Ti alloy, (d) Fe-0.67 mass% Ti alloy, (e) Fe-1.40 mass% Ti alloy, (f) Fe-2.11 mass% Ti alloy.

to be 1.43×10^{-21} kPa⁽⁹⁾. This suggests that the value of P_{O_2} was larger than the equilibrium dissociation pressure of TiO₂ formed on the alloys containing 0.67 mass% Ti or more. The presence of TiC and TiO₂ on the alloys containing 1.40 mass% Ti or more has to be kinetically explained rather than thermodynamically, indicating that these compounds can coexist under some kinetic conditions.

2. Oxidation behavior in air

From the above experiments, an oxide layer

formed on the surface is expected to exert a favorable influence on the retardation or the prevention of carbon deposition. We, therefore, investigated the oxidation behavior of iron-titanium alloys in air for 10.8 ks (3 h) at 1203 K and then studied the behavior of carbon deposition on the alloys during exposure to the 10%CH₄-H₂ mixture after the oxidation.

Mass gain curves of the specimens during the oxidation in air are shown in Fig. 4. In iron, as reported in the previous paper⁽⁶⁾, the

Fig. 3 X-ray diffraction patterns for as-polished specimens after the carburization. (a) iron, (b) Fe-0.09 mass% Ti alloy, (c) Fe-0.67 mass% Ti alloy and (d) Fe-1.40 mass% Ti alloy.

a: α -Fe, b: Fe_3C , c: carbon, d: TiC , e: TiO_2 (brookite).

Fig. 4 Effect of titanium on the rates of mass gain occurred by oxidation in air at 1203 K.

early stage of oxidation follows a parabolic rate law. However, departure from the parabolic rate occurs and the subsequent stage follows a linear rate law, suggesting that a rate-determining step in the oxidation of iron under this condition shifts from ionic diffusion in the scale to chemical reaction at an interface with time. The oxidation of iron-titanium alloys also follows the parabolic law in the reaction region except the initial stage where a continuous oxide layer may not form completely yet. Their parabolic rate constants are found to decrease markedly with increasing titanium content as shown in Fig. 5.

Typical X-ray diffraction patterns for surface of the oxidized alloys are illustrated in Fig. 6. Figure 6 shows that an oxide layer produced on iron consists of Fe_2O_3 , Fe_3O_4 , and FeO which seem to form in sequence from the exterior surface according to the equilibrium dissociation pressures of these oxides⁽⁹⁾ and that one of these oxides, FeO , disappears by small addition of titanium (0.09 mass%) and further addition of titanium up to 2.11 mass% causes the formation of $\text{FeO} \cdot \text{TiO}_2$ and TiO_2 besides Fe_3O_4 and Fe_2O_3 .

From the previous study⁽¹⁸⁾ on the oxidation of iron-titanium alloys in $\text{CO}-\text{CO}_2$ mixtures, the disappearance of FeO by small addition of titanium may be ascribed to the following fact: solubility of titanium to FeO decreases the concentration of quasi-free electron holes and

Fig. 5 Effect of titanium on the rates of oxidation in air at 1203 K. k_p : parabolic rate constant.

Fig. 6 X-ray diffraction patterns for the specimens after the oxidation. (a) iron, (b) Fe-0.09 mass% Ti alloy, (c) Fe-0.67 mass% Ti alloy and (d) Fe-1.40 mass% Ti alloy.

a: α -Fe, b: FeO, c: Fe_3O_4 , d: Fe_2O_3 , e: TiO_2 (rutile), f: $\text{FeO} \cdot \text{TiO}_2$.

retards its growth like chromium. Also, the solubility of titanium in the other iron oxides such as Fe_3O_4 and Fe_2O_3 may lead to a change in the characteristics of the oxides and hence to the retardation of diffusion of ions. A change in the characteristics of the oxides formed can also be observed in Fig. 7 where typical surface morphologies of the oxide layers are given; that is, their grain size evidently reduces with increasing titanium content. Also, the observations of cross sections of the specimens showed that their thickness decreases with titanium content. These indicate that higher titanium alloys form a denser and better adherent oxide layer.

3. Carbon deposition on pre-oxidized alloys

Figure 8 shows the rates of mass gain of the alloys when exposed to the 10% CH_4 - H_2 mixture at 1203 K after the oxidation in air. Let us note the process of carburization or carbon deposition here. Each of alloys containing 0.67 mass% Ti or less shows a sudden mass loss in the early stage and then a rapid mass gain, while the alloys containing 1.40 mass% Ti or more do not present such a drastic change. However, in comparison of the carburization process in Fig. 8 with Fig. 1, the rates of carbon deposition for the oxidized alloys increase markedly compared to that for the as-polished correspondents. This change in the mass gain curves is primarily ascribed to mass loss by reduction of iron oxides and to mass gain by carbon deposition.

Typical surface morphologies of the alloys after the reaction are shown in Fig. 9. It is observed from Fig. 9(a) through (c) that the deposition of filamentous carbon is obviously retarded with increasing titanium content. Also, as can be seen in Fig. 9(d) which shows the surface after removal of carbon, filamentous carbon deposits intensively on the spalling parts of oxides.

Typical X-ray diffraction patterns of the surfaces of the specimens after the reaction are given in Fig. 10. Figure 10 shows that non-reduced iron oxides (Fe_3O_4 and Fe_2O_3), α -Fe and Fe_3C coexist on the alloys containing 0.67 mass% Ti or less, whereas TiO_2 (rutile) besides them is present on the high titanium alloys containing 1.40 mass% Ti or more. However, $\text{FeO} \cdot \text{TiO}_2$ formed on the latter alloys during the oxidation is not detected. This indicates that it was reduced during the carburization. Alpha-Fe and Fe_3C seem to have formed during the reduction of iron oxides and the subsequent carburization, respectively. Also, TiO_2 (rutile) may not have newly formed during the carburizing process but the one formed during the oxidation only remained during the carburization because TiO_2 (brookite) forms in the 10% CH_4 - H_2 mixture without pre-oxidation as shown in Fig. 3 and mass gain of the oxidized alloys containing 1.40 mass% Ti or

Fig. 7 Typical morphologies of surfaces of the oxides formed on Fe-Ti alloys, showing the reduction of their grain size with increasing titanium content. (a) iron, (b) Fe-0.67 mass% Ti alloy, (c) Fe-1.40 mass% Ti alloy and (d) Fe-2.11 mass% Ti alloy.

more increases compared with that of the as-polished alloys. From Figs. 7, 9, and 10, the rapid increase in the rates of mass gain of iron and low titanium alloys in Fig. 8 is probably due to the formation of active iron by reduc-

Fig. 8 Mass gain curves of Fe-Ti alloys during oxidation in air and carburization in 10%CH₄-H₂ mixture at 1203 K.

tion of iron oxides and to the increase in the reaction area by spallation of the scale during the reduction; the active iron formed may promote the direct deposition of filmy carbon on the surface and filamentous carbon deposition through Fe₃C formation and decomposition. In other words, such a sudden mass gain in iron and low titanium alloys may have occurred because of the formation of loose and reducible unstable iron oxides on them. In contrast to that, since a dense and adherent stable oxide, TiO₂, remains on the alloys containing 1.40 mass%Ti or more even during carburization as shown in Fig. 10, carbon deposition on the alloys must have been retarded, although the amounts of carbon deposition increase compared with those on the as-polished alloys because of the coexistence of reducible iron oxides.

These experiments suggest that addition of titanium to iron is very effective for the retardation of carbon deposition if it is possible to

Fig. 9 Scanning electron micrographs of the specimens after the carburization in 10%CH₄-H₂ mixture following oxidation in air at 1203 K. (a) iron, (b) Fe-0.67 mass% Ti alloy, (c) Fe-2.11 mass% Ti alloy and (d) Fe-0.67 mass% Ti alloy, showing the surface after removal of filamentous carbon.

Fig. 10 X-ray diffraction patterns for the specimens after the carburization in 10%CH₄-H₂ mixture at 1203 K. (a) iron, (b) Fe-0.67 mass% Ti alloy and (c) Fe-1.40 mass% Ti alloy. a: α -Fe, b: Fe₃C, c: carbon, d: Fe₃O₄, e: Fe₂O₃, f: TiO₂ (rutile).

form the thin film of only TiO_2 in the atmospheres with low partial pressures of oxygen.

IV. Conclusions

Titanium retarded carburization and carbon deposition by changing the microstructure of the alloys from austenite to ferrite and by forming a stabler carbide (TiC) than Fe_3C .

TiO_2 (brookite) formed on as-polished alloys containing 0.67 mass% Ti or more even in the 10% CH_4 - H_2 mixture, so that carbon deposition was markedly retarded on the alloys. Under this condition, TiO_2 may have formed by the reaction of titanium in the alloys with small amounts of oxidizing gases such as O_2 and H_2O present in the atmosphere.

On oxidation in air, Fe_2O_3 , Fe_3O_4 and FeO formed on iron in sequence from the exterior surface and small addition of titanium (0.09 mass% Ti) retarded the formation of FeO and a further addition of titanium up to 2.11 mass% caused the formation of $\text{FeO} \cdot \text{TiO}_2$ and TiO_2 (rutile) besides Fe_3O_4 and Fe_2O_3 . The reason why brookite or rutile formed in carburizing gas or in air, respectively, could not be clarified.

When exposed the alloys containing 0.67 mass% Ti or less to the 10% CH_4 - H_2 mixture after the oxidation in air, a rapid mass gain by carbon deposition occurred. It is probably due to the formation of active iron by reduction of iron oxides and to the increase in the reaction area by spallation of the scale during the reduction. However, carbon deposition on high titanium alloys containing 1.40 mass% Ti or more was considerably retarded because TiO_2 formed during the oxidation remained on the surface even during carburization, although the amounts of carbon deposition increased

compared with that on the as-polished alloys owing to the coexistence of reducible iron oxides.

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