Effects of Alloying Elements on High-Temperature Oxidation Behavior of Fe-Si Alloys

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Introduction

At high temperatures, most metals will be oxidized under a various conditions of atmospheres. Therefore, the issue of understanding the oxidation behavior has always been focused to overcome metal oxidation problem through the studies on the rate of the oxidation reaction, and methods of controlling scale morphology.

Carbon steel is produced in very large quantities worldwide. Usually it is cast into pieces of slabs and subsequently reheated to around 1000 – 1200°C to be hot-rolled to various thickness. During the reheating operation at high temperatures, in oxidizing gases, it causes growth of a thick iron oxide scale on the steel, which consumes about 1-2% of the total amount of steel. This high amount of oxide scale which later needs to be removed in the production process, can gives impact on the production cost economically.

Currently, the rapid development of new technologies has somehow made people to demand better and efficient technologies which could greatly benefit them. In the case of automotive industry, people are now demanding for energy saving in automobiles, specifically increasing the fuel efficiency. A lighter automobile is one of the options to fulfill this demand. This solution can be achieved by simply reducing the thickness and weight of structural metal sheet parts, but it creates another problem. The weight reduction leads to decrement in steel strength. Therefore, an addition of Si can help to compensate the losing strength of this structural steel.

High Si steels are highly demanded especially in automotive industry as it has a good balance between ductility and strength. In addition to that, a proper scale removal prior to hot rolling process is needed to obtain a good surface finish. However, with the dissolution of Si into the steel, a quality surface finish is hardly to be accomplished as SiO₂ is easily to form on the steel surface and some parts still remain on the substrate surface after the scale removal process. Therefore, the external formation of Si oxides must be suppressed to achieve the desired surface finish. Thus, addition of alloying elements is a good possibility to suppress the formation of external Si oxide scale. The high-temperature oxidation behavior of Fe-Si alloys containing Mo and/or Al is clarified.

Experimental Procedure

As-received Fe-Si alloys with 0.1, 0.3, 0.5mass%Mn, 0.2, 0.5mass%Mn, 0.2mass%Al content were cut into dimensions of about 10 X 10 X 1mm. The specimens were polished down using various grades of SiC paper up to the grit of #1500 and diamond-polished until mirror finish was obtained. Then, ultrasonic cleaning in an ethanol solution was done prior to oxidation test. The high temperature oxidation tests were
conducted in 2 phases. The 1st phase was done for 5 to 180 min at 1150°C and 1200°C in a N₂-3%O₂-20%H₂O atmosphere, and 2nd phase test was performed in N₂-H₂ atmosphere for 60 min at 900°C. In 2nd phase test, Fe-Si alloys with removed outer oxide scale formed at 1150°C and 1200°C, were used. In addition, specimens were also heated in N₂-H₂ without underwent 1st phase oxidation.

Optical Microscope (OM), Scanning Electron Microscope (SEM) and Electron Probe Micro Analyzer (EPMA.) were used for observation and analysis. After 1st phase oxidation test were conducted, the specimens’ weight were measured to determine the mass gain oxidation kinetics. The specimens’ surface was photographed prior to mounting. After mounted in the mould, the specimens were cross-sectionally cut and again were polished and diamond-polished until mirror-like finish was obtained. Then, the cross-sectional images of oxidized specimens were observed by OM and then elemental mapping were conducted using EPMA.

After 2nd phase oxidation test were conducted, these specimens’ surface were observed using OM. Next, they were mounted in mould and cross-sectionally cut. The cut specimens were polished and diamond-polished until it obtained mirror finish. EDS mapping and point analysis were executed on the cross-section of the oxidized specimens.

Results and Discussion
Oxidation in N₂-O₂-H₂O

The oxidation kinetics of high Si steels at 1150°C is shown in Fig. 1. From the data obtained, it is found that generally all specimens are approximately following a linear rate oxidation law. The base steel (No. 1) experienced highest weight gain compared to other specimens. The weight gain of specimens with Mo addition (no. 3-7) decreases as Mo content increases, and similar behavior is observed with Al addition; higher Al content contributed to a lower weight gain. Specimen No 13 which contains both Mo and Al has the lowest weight gain.

At 1150°C, the scale formed is generally consisting of outer scale of Fe oxides, inner scale of Si-Mn rich oxide layer and internal oxidation zone containing Si-Mn oxides. In general, longer oxidation time led to the formation of thicker scales externally and internally regardless of type of samples. Base steel (No.1) formed a thick and dense Fe-oxide scale, and continuous Si-rich oxide layer.

At 1200°C, all specimens formed a non-uniform outer scale, suppression of inner oxide layer, thinner internal oxidation zone and significant increase in oxidation weight gain. At this temperature, Fe₂(Si,Mn)O₄
forms a liquid phase with FeO (eutectic), and the liquid phase penetrates into grain boundaries of the Fe oxides scale. Addition of Mo led to the formation of complex-structure containing Mo oxide and fayalite at scale-substrate interface. On the other hand, addition of high Al content results in formation of non-continuous eutectic Si-rich layer. Last but not least, Fe-Si alloy containing both Mo and Al (No.13) has produced a thinner outer scale than other specimens, maybe due to the presence of Al in the eutectic FeO-Fe$_2$SiO$_4$ phase as shown in Fig. 3.

**Heating in N$_2$-H$_2$**

After steels were oxidized at 1150°C, the oxide scales were partly removed from the steel. Then, the specimens were reheated at 900°C in N$_2$-H$_2$ atmosphere. Generally the scale consists of 3 parts namely metallic Fe on the top layer, Si-Mn rich oxide layer in the middle and followed by internal oxides of Si and Mn in the substrate. Si-Mn rich layer, which is still remained on the base steel, formed a continuous layer, while in the Mo and Al added steels, the scale on substrate was a mixture of metallic Fe and fayalite layer. With addition of both Mo and Al, the presence of Al is detected in substrate-scale interface and IOZ.

Specimens which were firstly oxidized at 1200°C show similar characteristics to those at 1150°C, which are the presence of remained Si-Mn rich layer liquid phase and Fe in metallic form, and formation of internal Si and Mn oxides. The depth of IOZ is roughly same for steels containing Mo and Al. With addition of both Mo
and Al, the formation of IOZ is more extensive with the presence of Al detected in the area as shown in Fig. 4.

In the case of specimens heated in N$_2$-H$_2$ atmosphere without undergo any oxidation process in prior, Si and Mn internal oxides are formed in the surface of all specimens. For the base steel, the concentration of Si and Mn internal oxides near the surface is low. Inversely, for Mo and/or Al added steels, the concentration of Si and Mn internal oxides are higher.

**Conclusion**

In 1$^{st}$ phase oxidation, oxidation at 1200$^\circ$C generally leads to formation of non-uniform outer scale, suppression of inner oxide layer, thinner internal oxidation zone, and significant increase in oxidation weight gain. Also, longer oxidation time led to the formation of thicker scale externally and internally regardless of type of samples.

Addition of high Mo resulted in the formation of a porous fayalite and Fe oxides scale at 1150$^\circ$C, and formation of duplex-structure scale containing Mo oxide and fayalite in substrate-scale interface, at 1200$^\circ$C. Addition of 0.5%Al resulted in increment of continuous Si-rich layer thickness and IOZ thickness at 1150$^\circ$C. Moreover, addition of 0.3Mo-0.2Al led to formation of extensive IOZ at 1150$^\circ$C and suppression of Si-rich layer at both temperatures, but rough scale-substrate interface.

In 2$^{nd}$ phase oxidation, in general FeO is reduced to metallic Fe in all samples. However, fayalite layer is still remained and could not be reduced. Addition of both Mo and Al led to the formation of a thicker internal oxidation zone consisting of Si and Mn oxides and segregation of Al oxide in the front of internal oxidation zone (IOZ).