Investigating the oxidation behavior of carbon steel in fire scene: a new method for fire investigations

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ABSTRACT: A major component of fire investigation is tracking the cause of fire, finding of which help to strengthen the physical evidence, especially in case of arson with accelerants. When metallic substances are exposed to fire at high temperature, they undergo oxidation. Accelerants at the fire scene impart some oxidative characteristics on metallic materials. For instance oxides and substrates found on metal surfaces provide valuable information for determining the characteristics of fire, such as exposure temperature, duration and involvement of a liquid accelerant. In this study, we investigated the oxidation behavior of carbon steel at high temperature in a simulated flame environment using ethanol combustion. After oxidation, the morphological and microstructural features of the samples were characterized by observation, scanning probe microscope, X-ray diffractions and scanning electron microscopy with energy-dispersive spectroscopy analysis. The results showed that elemental carbon was deposited on the samples surface, which were ascribed to the incomplete combustion of ethanol. An oxide with a mesh-like pattern appeared on the samples, which was ascribed to the complex oxidation conditions of the fire scene. The properties of the oxides were strongly dependent on the oxidation duration, temperature and atmosphere. These results provide reference information for determining the presence of combustion accelerants at the fire scene.

KEYWORDS: fire investigation, arson, carbon steel, ethanol, oxidation

INTRODUCTION

In legal disputes, high quality evidence based on scientific methods is desirable. In case of fire-related matters, the evidence found at the fire scene must be analyzed correctly and interpreted accurately [1]. In order to accurately identify the origin and cause of the fire, fire investigators need to collect all related traces of evidence and perform comprehensive scientific analysis. However, this is very challenging in some cases due to the complex nature of fire scenes, especially in cases where the physical evidence is easily damaged or difficult to extract. It is difficult to establish the cause of arson since the motivation for arson is often complex. In most instances, arson is started by ignitable liquid accelerants [2,3]. One of the major tasks of fire investigators at the crime scene is to collect the fire debris which contains traces of ignitable compounds [3,4]. Chemical analysis is one of the most widely used techniques by fire investigators. Some scholars propose that GC-MS can be used to analyze

traces of ignitable compounds such as gasoline, medium-petroleum fractions, and heavy petroleum distillates from fire residues [5, 6]. Recent advances in methods of extracting and analyzing information such as gas chromatography have enabled the determination of biodiesel in fire residues [2]. The American Society for Testing and Materials (ASTM) recommends some methods for fire debris analysis [7–9]. However, the accuracy of these methods in chemical analysis depends on the purity of the samples. In the case of samples obtained from burning scenes, volatile fuels, such as gasoline and ethanol, may be difficult to analyze [10, 11]. The complex environment at fire scenes produces different oxidation characteristics on metals [12]. In a fire scene, the oxidative products generated by the combustion of liquid accelerants will promote oxidation of metallic substances. This oxidation is affected by type of combustion accelerant and burning duration and other factors such as the thickness, composition, surface pattern and color of
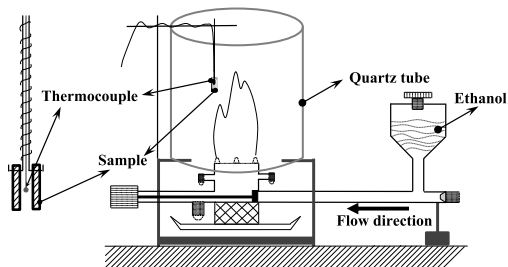
Fig. 1 The device that simulated ethanol-combustion atmosphere.

Table 1 Chemical composition of carbon steel (wt., %).

C	Mn	Si	S	P	Fe
0.15	0.30	0.30	0.045	0.045	Bal.

Bal. = balance; the elements are iron except the other elements.

the metal oxide layer. Therefore, it is important to investigate arson and to clarify the relationship between the type of liquid accelerant, combustion duration and the oxidation behavior of metallic surfaces, to provide information to guide for fire investigation [13–15]. Carbon steel and ethanol are widely used in many aspects of our daily lives. In this study, a laboratory device simulated ethanol-combustion atmosphere was established and high-temperature oxidation properties of carbon steel were investigated.

EXPERIMENTS

Vaporizing ethanol was used to create a laboratory simulated ethanol-combustion atmosphere. The schematic diagram of the device is shown in Fig. 1. The temperature curve for the combustion process was developed by a K-type thermocouple. The material used in this research is carbon structural steel which is widely used in many aspects of our lives, and its nominal chemical composition is provided in Table 1. Carbon steel ingot was precision-machined into $3 \times 10 \times 20$ mm sections which were cut using electrical discharge machining (WEDM). A hole with 2 mm diameter was cut by WEDM at one end to hang the sample, and then ground with 2000 grit SiC sand paper. The samples were subsequently cleaned in an ultrasonic bath of acetone, rinsed with ethanol and distilled water. It was dried, weighed and their sizes were measured. Finally, the samples were put in the drying oven and spared. The positioning of the sample and thermocouple during the oxidation test is shown in Fig. 1. The
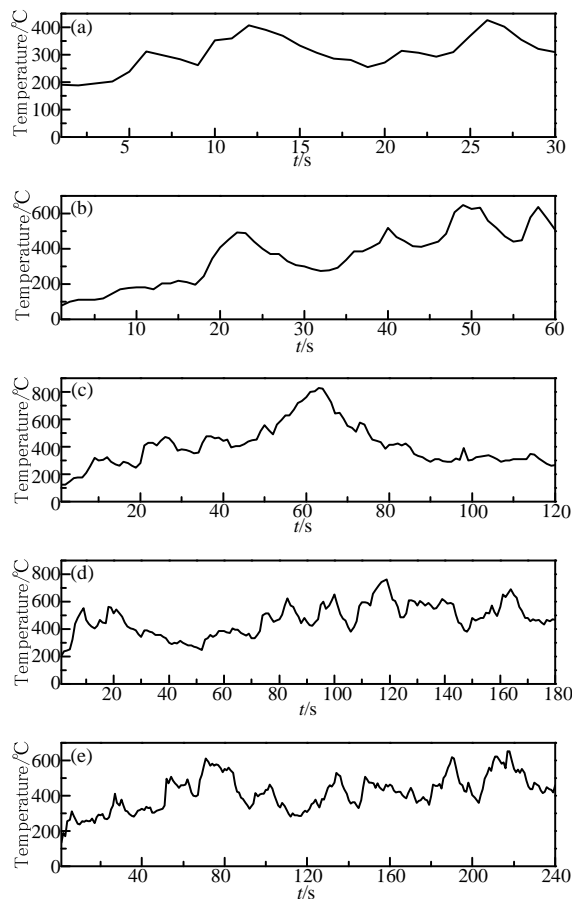

Fig. 2 Temperature curve of oxidation time at (a) 0.5 min, (b) 1 min, (c) 2 min, (d) 3 min and (e) 4 min.

experimental duration was 0.5, 1, 2, 3, and 4 min, and the temperature curve is provided in Fig. 2.

After oxidation, the surface morphology and microstructure of the carbon steel were examined with a scanning electron microscope (Leo 1530 FEG SEM, Carl Zeiss SMT Ltd) at an accelerating voltage of 20 kV and scanning probe microscope (CSPM5500, Being Nano-Instruments Ltd). The phase composition of the oxide layer was analyzed using energy dispersive X-ray spectrometer (INCA EDS, Oxford Instruments) and X-ray diffractometer (XRD-6100, Shimadzu).

RESULTS AND DISCUSSION

Carbon steel undergoes different levels of oxidation when exposed to laboratory simulated ethanol-combustion atmosphere for different durations. In the study, the color of the samples changed during the oxidation process (Fig. 3), probably due to formation of different oxides on the samples [16].
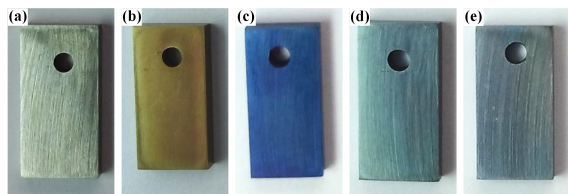
Fig. 3 Visual analyses of the samples after exposure to ethanol containing gas at (a) 0.5 min, (b) 1 min, (c) 2 min, (d) 3 min, and (e) 4 min.
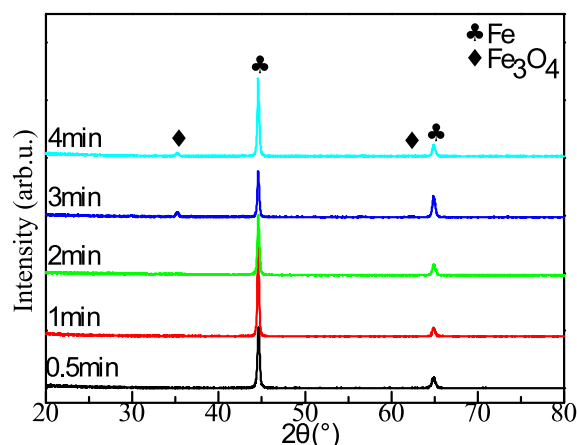

Fig. 4 X-ray diffraction results of carbon steel at ethanol oxidation atmosphere.

The color of the sample surface (Fig. 3de) did not significantly change when the oxidation time exceeded 3 min, indicating that the level of oxidation gradually becomes stable. This phenomenon varies with oxidation time and chemical composition of the surface oxide. During the oxidation process, carbon
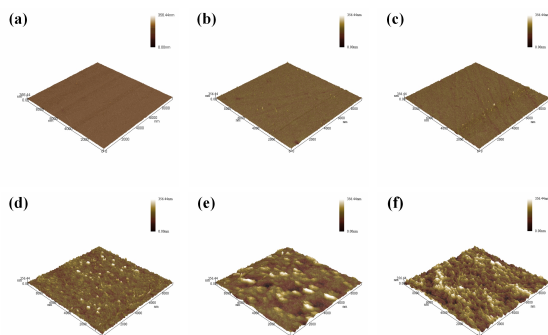

Fig. 5 Scanning probe microscope analysis of the samples after oxidation at (a) 0 min (unoxidized), (b) 0.5 min, (c) 1 min, (d) 2 min, (e) 3 min, and (f) 4 min.
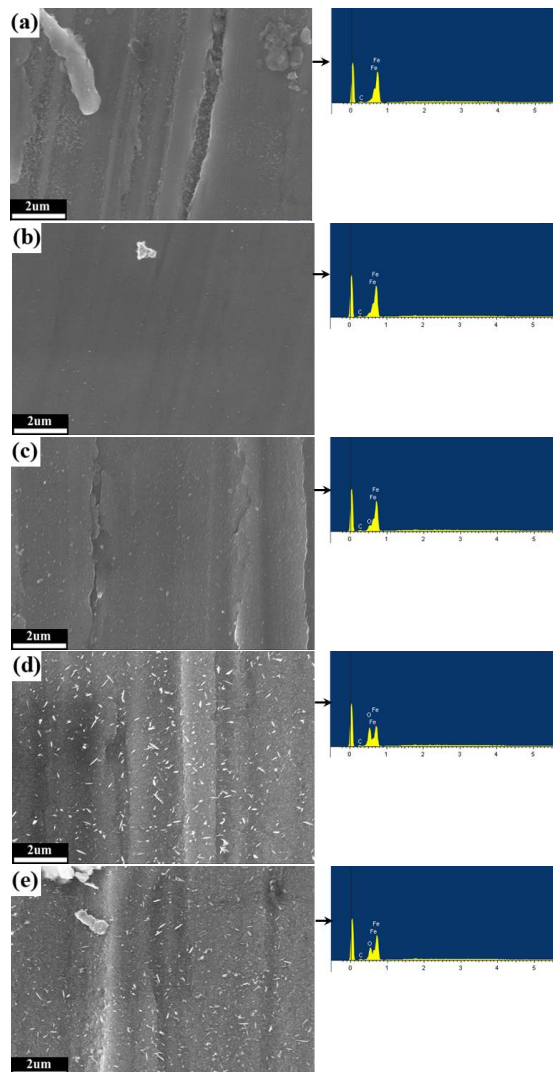

Fig. 6 SEM surface morphology of the samples after oxidation at (a) 0.5 min, (b) 1 min, (c) 2 min, (d) 3 min, and (e) 4 min.

steel materials will form three main components of iron oxide, namely, wustite (FeO), magnetite (Fe_3O_4) and hematite (Fe_2O_3), with different colors [16]. Interestingly, oxidation in the presence of water vapor also produces a variety of $FeXOY \cdot zH_2O$ compounds, with varying colors. Visual analysis shows that the color pattern of the alloy after exposure to high temperature depends on the oxides of Fe. The contents of oxides formed under different oxidation stages display different colors on the sample surface along the oxidation process. The presence of polishing marks on the metal surface is due to a thin oxide film [13]. The X-ray diffraction analysis showed that magnetite (Fe_3O_4) oxides were

formed on the sample surface when the oxidation duration exceeded 3 min (Fig. 4). In general, the oxide layer formed on carbon steel was oxidized at high temperatures consisted of wustite, magnetite, and hematite. In fact, the high mobility of defects in wustite (FeO) renders this layer to be thicker compared with the magnetite and hematite layers [17]. However, wustite oxides were not found in this study, which may be ascribed to the rapid oxidation caused by strong oxidizing agents present in the ethanol-combustion atmosphere. Interestingly, analysis of the mass changes of samples by thermogravimetric analysis showed a significant weight loss probably caused by the rapid shedding of the oxide layer by the flow of air during the combustion process. The scanning probe microscope revealed that exposure to oxidation for less than 1 min did not cause significant oxidation on the metal surface compared to the unoxidized state. Notably, only few spot-like white oxides were detected on the sample surfaces (Fig. 5bc). There was a correlation between the different oxides formed on the samples surface and the change in color of samples (Fig. 3). A scanning electron microscope revealed that there was no significant oxidation on the metal surface when the oxidation duration was less than 2 min (Fig. 6abc). But a small amount of white spot oxide particles was observed, which is in good agreement with results of the scanning probe microscope. The amount of white oxide formed on the metal surface is increased with the retention time. Moreover, needle-like oxides were formed on the sample surface when the oxidation duration was more than 3 min (Fig. 6de), and the oxide did not completely cover the sample surface, as revealed by SEM analysis. The mapping results of the EDS shown in Fig. 6 demonstrate that elemental carbon was deposited on the sample surface, which could be due to incomplete combustion of the accelerants. This observation can be used to determine the presence of a combustion accelerant in a fire scene.

During oxidation, a mesh-like pattern was formed on the sample surface, and this pattern was enlarged at the surface defect of the samples when the oxidation duration was 2 min (Fig. 7a). The sample surface was covered by a mesh-like oxide when the oxidation time was extended to 5 min as shown in Fig. 7d. Fig. 7bc show that oxidation is initiated at the defect site on the sample surface, leading to more intense oxidation around it. Notably, the oxidized mesh-like pattern expands outward from the defect. It is related to the large surface energy of defects, which leads to preferential
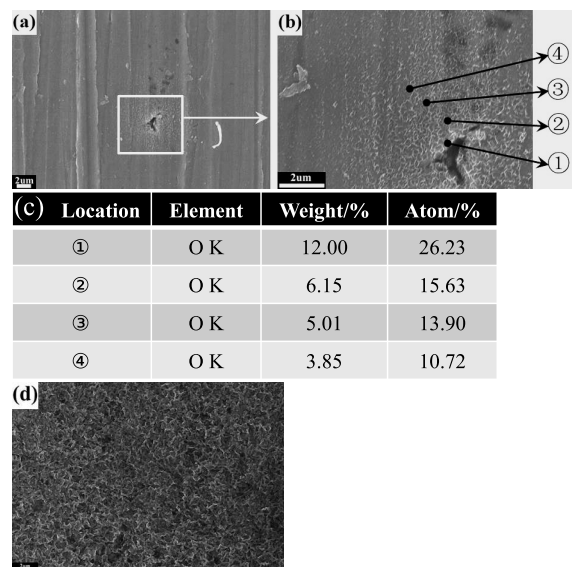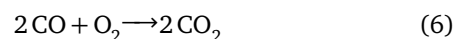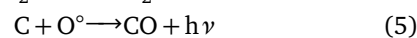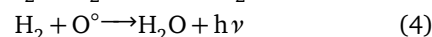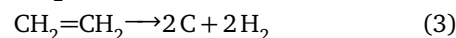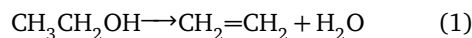

Fig. 7 The SEM and EDS result of samples exposed in laboratory simulated ethanol-combustion atmosphere for 2 min (a,b) and 5 min (d).

Location	Element	Weight/%	Atom/%
①	O K	12.00	26.23
②	O K	6.15	15.63
③	O K	5.01	13.90
④	O K	3.85	10.72

oxidation. The mesh-like pattern may be caused by the grain boundary of the samples.
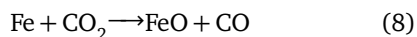
The oxidation of carbon steel in a laboratory simulated ethanol-combustion atmosphere is characterized by oxidation accompanied with the deposition of carbon and with the formation of a mesh-like pattern of oxides on the sample surface. In oxygen-deficient environments, ethanol often undergoes incomplete combustion and pyrolysis according to equations (1)–(6) [18–21], which produces H_2O, CO_2, CO, and C.

$$CH_3CH_2OH \longrightarrow CH_2{=}CH_2 + H_2O \qquad (1)$$
$$O_2 + h\nu \longrightarrow 2O^\circ \qquad (2)$$
$$CH_2{=}CH_2 \longrightarrow 2C + 2H_2 \qquad (3)$$
$$H_2 + O^\circ \longrightarrow H_2O + h\nu \qquad (4)$$
$$C + O^\circ \longrightarrow CO + h\nu \qquad (5)$$
$$2CO + O_2 \longrightarrow 2CO_2 \qquad (6)$$

The EDS results (Fig. 6) indicated that carbon was formed on the sample surface, which is ascribed to the pyrolysis of ethanol. Reactions shown in (4) and (5) would compete with each other under oxygen deficiency conditions. The ΔG°-T plot shows that H_2 is preferentially reactive at temperatures below 630 °C [22]. However, in this study, the temperature range is small, therefore, it can be determined thermodynamically, that elemental carbon deposition occurs during incomplete combustion.

Chain reactions in the combustion process proceed at a high rate, and H_2 is produced as an intermediate product. H_2 reacts with oxygen to form water thereby accelerating metal oxidation, or dissolves in oxides to form H(ox) which enhances ion diffusion and accelerates the formation of oxide layer [23]. The final result is accelerated oxidation of the metal and porous oxide layer [24].

The combustion products, H_2O and CO_2 create a highly oxidizing atmosphere enhancing the oxidation of carbon steel [25–27]. The initial step is the adsorption of the active gas to the metal surface followed by oxide nucleation and growth. The reactions (7) and (8) may occur depending on the atmospheric conditions [28, 29].

$$Fe + O_2 \longrightarrow FeO \qquad (7)$$
$$Fe + CO_2 \longrightarrow FeO + CO \qquad (8)$$

The $H_2O_{(g)}$ generated during combustion undergoes cathodic depolarization with Fe to form FeOOH at high temperature [28]. The Fe^{2+} produced from the reaction activates anhydrous ethanol pyrolysis of carbon nanotubes [30–32]. On the other hand, the $H_2O_{(g)}$ produced during combustion inhibits the dehydration reaction of FeOOH, causing it to react with Fe^{2+} forming magnetite (Fe_3O_4), as indicated by the XRD results (Fig. 4).

Elemental carbon was observed on the sample surface, which could be due to incomplete combustion of ethanol, equation (3). The carbon formed during combustion is composed of multi-layered graphite molecules [33]. Several studies have shown that Fe^{2+} has a specific catalytic effect on the thermal decomposition of anhydrous ethanol which leads to the formation of carbon nanotubes when the temperature exceeds 600 °C [26]. The carbon molecules formed on samples surface can be cleaned by ultrasonication with ethanol, which may be the paragenesis of oxide and carbon. This is different from the soot on the metal surface formed during combustion. Further research is needed to explore this concept.

CONCLUSION

Cases of arson have received widespread attention in recent years. In this study, the oxidation behavior of carbon steel metal surface was used for fire investigation. The high-temperature oxidation behavior of carbon steel was studied at different duration in a laboratory simulated ethanol-combustion atmosphere. The morphology, microstructure and composition of metal oxides were comprehensively analyzed, as well as the correlation with the oxidation characteristics at different exposure conditions. The laboratory results showed that mesh-like patterns were formed on the surface of carbon steel, which began from the defect sites on the surface of substrate. Due to oxidation in the laboratory simulated ethanol-combustion atmosphere, the pyrolysis of ethanol deposited elemental carbon molecules on the surface of carbon steel. These findings offer valuable information for investigating the causes of fire, as well as determine whether combustion accelerants are present at fire scenes to provide evidence for court cases related to arson.

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