

Microstructure and High Temperature Oxidation Behavior of Aluminum Alloyed Cast Irons

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Abstract

The present study postulates the phases formed/oxidation resistance of aluminum alloyed cast irons (0 to 4 wt% Al) based on scanning electron microscopy, energy dispersive X-ray spectroscopy (EDS), X-ray diffraction and oxidation test. Mechanisms of the oxidation of the alloys were determined at high temperatures (700-1000 °C). A direct relationship between Al content and oxidation temperature was found; at a lower oxidation temperature (less than 800 °C), low oxidation resistances were obtained characterized by formation of FeO, Fe₃O₄ and Fe₂O₃. With increasing the Al content, the performance of the alloys enhanced noticeably. Scale thickness was reduced progressively with increasing aluminum content. Under all testing conditions, the oxidation kinetics is parabolic with different parabolic rate constants.

Keywords: Aluminum alloyed cast irons, Oxidation resistance, Phases, Oxidation kinetics

1. Introduction

Prolonged services at elevated temperature require combination of properties that would be difficult to achieve without addition of special alloying elements. The addition of suitable alloying elements to cast irons is the most important way to protect them against high temperature oxidation and scaling (Li, Perrin, Burger, McFarlan, Black, Logan and Williams, 2004). When the protective scale are adherent and non porous, the oxidation process will be inhibited and progressive process of oxidation will be prevented. Many elements, such as Si, Cr, and Al provide this protective layer for alloyed cast irons (Pint, Tortorelli, and Wright, 1999; Xu, Ferry, and Wang, 2005).

Cast irons containing aluminum show excellent oxidation resistance by causing the formation of an adherent aluminum-rich oxide films. Cast irons alloyed with aluminum form a thin, tightly adhering oxide film on the surface that inhibits further oxygen diffusion into the substrate. Due to similar graphitization effect of aluminum and silicon, in some types of alloyed cast irons, aluminum replaces much of silicon that is normally present in cast irons. In other types of cast irons, aluminum is added as an alloying element in addition to the normal silicon content (Smickley and Rundman., 1981). The elevated temperature properties of the aluminum cast irons are enhanced appreciably by the addition of one to two percent of molybdenum. Combination of high silicon plus aluminum and molybdenum produces ductile cast irons with excellent qualification for high temperature applications (Rana, Khan, Amjad, and Abbas, 2001).

Hardwick and Wallwork (1978) illustrated that sufficient quantities of chromium, aluminum, or silicon must be presented in an alloy to ensure that protective oxide (Cr₂O₃, Al₂O₃, SiO₂) are formed on exposure to oxidizing environments. Aluminum scales appear very attractive, particularly at high temperatures due to reducing cations diffusion through scale and its high free energy formed (greater than that of Cr₂O₃). Aluminum-forming cast iron alloys are good candidates to resist high temperature oxidation atmospheres because alumina scales, especially α -Al₂O₃, exhibits excellent resistance; these scales acting as diffusion barriers during the oxidation process at

high temperatures (Chevalier¹, Houngninou¹, Paris, Bernard¹, Gaffet, Munir¹, Larpin and Borchardt, 2003). The industrial boiler casting produced from cast irons containing 5-7% aluminum, with 0.7-1.0% C, exhibits 6-8 times longer life than the medium silicon heat resistant ductile cast irons at operating temperature of about 1000 °C (Sun, and Wang, 1996). (Kiani Rashid and Edmonds, 2003) found that in cast irons containing aluminum a very thin and adherent film of aluminum oxide is produced at the short period of heating. It protects the bulk of the alloy from the further attack and the average thickness of iron-rich oxide layers decrease as the aluminum content increases. The present study is mainly concentrates on the effect of aluminum content on the phases formed and the oxidation resistance relationship.

2. Experimental Procedure

Three cast iron alloys contain different amount of aluminium were produced using silica lined coreless induction furnace. The liquid alloys were poured at temperatures between 1350 and 1400 °C in a sand mold to produce 200 mm long x 25 mm diameter test bars. The chemical composition of the alloys studied is listed in Table 1.

For Oxidation tests, circular shape specimens with dimensions of 20 mm diameter x 4.5 mm thick were sectioned from test bars (ASTM G54-84, 1988) (Nicholls and Bennett, 2000). They were degreased with acetone and ultrasonically cleaned. Microbalance with accuracy ± 0.1 mg was used to determine the weight gain. Oxide surfaces were examined using optical microscopy (OM) and scanning electron microscopy (SEM). High temperature isothermal oxidation experiments were carried out in a muffle furnace in static air. The specimens were oxidized at temperatures of 700, 800, 900, and 1000 °C at interval time up to 100 hrs. The specimens were weighed periodically, every 5 hrs. X-ray diffraction was carried out to determine the phases formed in Al-free cast iron and aluminum alloyed cast irons before and after oxidation tests.

3. Results and Discussion

The microstructural analysis using optical microscopy, scanning electron microscopy (SEM) equipped with energy dispersive spectrometer (EDS) and X-ray diffraction (XRD) of as cast irons with different content of aluminum show indication of different phases formed. Some of these analyses are shown in Fig. 1. Different shapes, sizes and distribution of structural elements were found. Structural effects were dominated by a significant increase in percent of ferrite at high level of aluminum content. The different phases found were mainly α -iron, graphite and pearlite. Analysis of cast iron with 2.7 and 4.0% aluminum indicate that ferrite is the main matrix component with graphite in the flake shape. Graphite morphology and its distribution were different from non-alloyed cast iron. Evidence of existing of more volume fraction of pearlite as aluminum percent was increased. Different hardness levels can be related to the variation in their microstructure; it shows the dependence of hardness on aluminum content. Matrix free from carbide formed in alloys contain aluminum content up to 4.0% shows a relatively low hardness (220-360 HV); this is a result of the predominant ferrite phase with identification of different amounts of pearlite.

It was found that the first stage of oxidation normally starts by the oxidation of graphite flakes exposed to oxidizing air environment, then followed by oxidation of exposed alloying elements. In this period, if weight change is directed to a negative weight loss. This could be due to the high rate of carbon oxidation compared to metal oxidation. In the followed stage of oxidation, normally the weight gain by formation iron oxide scales prevails over the weight loss by decarburization. The oxidation kinetics observed for alloy I without Al can be ascribed to the combined effects of iron oxide accumulation (weight gain); the weight losses were due to the decarburization (Fig. 2). When the consumption of graphite at the surface exceeds the relative weight gain due to oxidation of iron, the weight change tends to be negative. While in the exceeding of weight gain due to oxide formation more than decarburization, the total weight change starts increasing. It is believed that cavities or gaps are left after graphite consumption, but iron oxides could fill these holes and thereby provide anchors that could key the scale to the metal. The scale cracking and spallation or partial spallation can cause the fluctuation in the weight change rate.

The existence of cracks in the oxide layer caused a rapid increase in the surface area in contact with oxygen and then accelerates the oxidation kinetics (Fig. 3). It was noted that after the first stage of oxidation period at 900 and 1000 °C the scale formed on the alloy I tends to spall from the surface on cooling. When the scale spalled away, the surface oxidized again and scale appears more adherent to the subsurface. The scale formed on oxidized cast iron at high temperatures is composed of different layers consist of different types of iron oxides; FeO, Fe₃O₄ and Fe₂O₃.

Figures 4 and 5 show that oxide layers formed on the surface of alloys II and III (2.7 and 4% Al) are expected to exert a favorable influence on the retardation of the oxidation. The oxidation of low aluminum cast irons were controlled by outward diffusion of iron ions in the scale and that the oxidation rates decrease with increasing

aluminum content. The solubility of aluminum in iron oxides leads to a change in the characteristics of the oxide and hence to the retardation of diffusion of iron ions. As in other alloyed cast iron, external protective scales are formed initially; these scales suffer cracking and spalling within a short period. Subsequently, a second or a third scale were observed which affects the oxidation rate (Fig. 6). Small particles are released from the specimens; this gives an evidence of oxide behavior of the alloy.

The oxidation processes followed parabolic rate law. The parabolic rate constant (k_p) for alloy II and alloy III, have the same tendency to increase the oxidation rate with temperature. The parabolic rate constants for 2.7 and 4.0 % aluminum alloys at 700 °C are 1.43×10^{-10} and 1.04×10^{-10} g²/cm⁴/s respectively. While at 1000 °C the k_p values for the same alloys are 3.35×10^{-7} and 2.16×10^{-7} g²/cm⁴/s respectively. It is obvious that oxidation kinetic is less affected when the aluminum content is low. The oxidation tendency in these low aluminum content cast irons increases with temperature. The reason for voids and cracks formation may be attributed to differential contraction of the oxide scale and metal during thermal cycling. The oxide formation along the graphite flakes and penetration of gases to cast iron can cause increase in volume which promotes voids and cracks formation.

4. Conclusions

- 1) The changeable graphitization potential of aluminum in cast iron results in producing aluminum alloyed cast irons with different and various properties.
- 2) Aluminum has a significant role in altering microstructure condition. Matrix structure contains various proportions of ferrite, pearlite and graphite.
- 3) For aluminum alloyed cast irons there is no indication of spall at temperature range between 700 and 800 °C. Oxidation rate of aluminum alloyed cast iron tends to decrease with increasing aluminum content.

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Table 1. Chemical composition of aluminum cast irons (wt%)

Sample No.	Chemical Composition							
	Al	C	Si	S	P	Mn	Ni	Cr
I	0.0	3.23	2.1	0.05	0.09	0.38	0.05	0.41
II	2.7	4.02	1.79	0.04	0.07	0.37	0.06	0.55
III	4.0	3.9	1.72	0.03	0.09	0.33	0.04	0.52

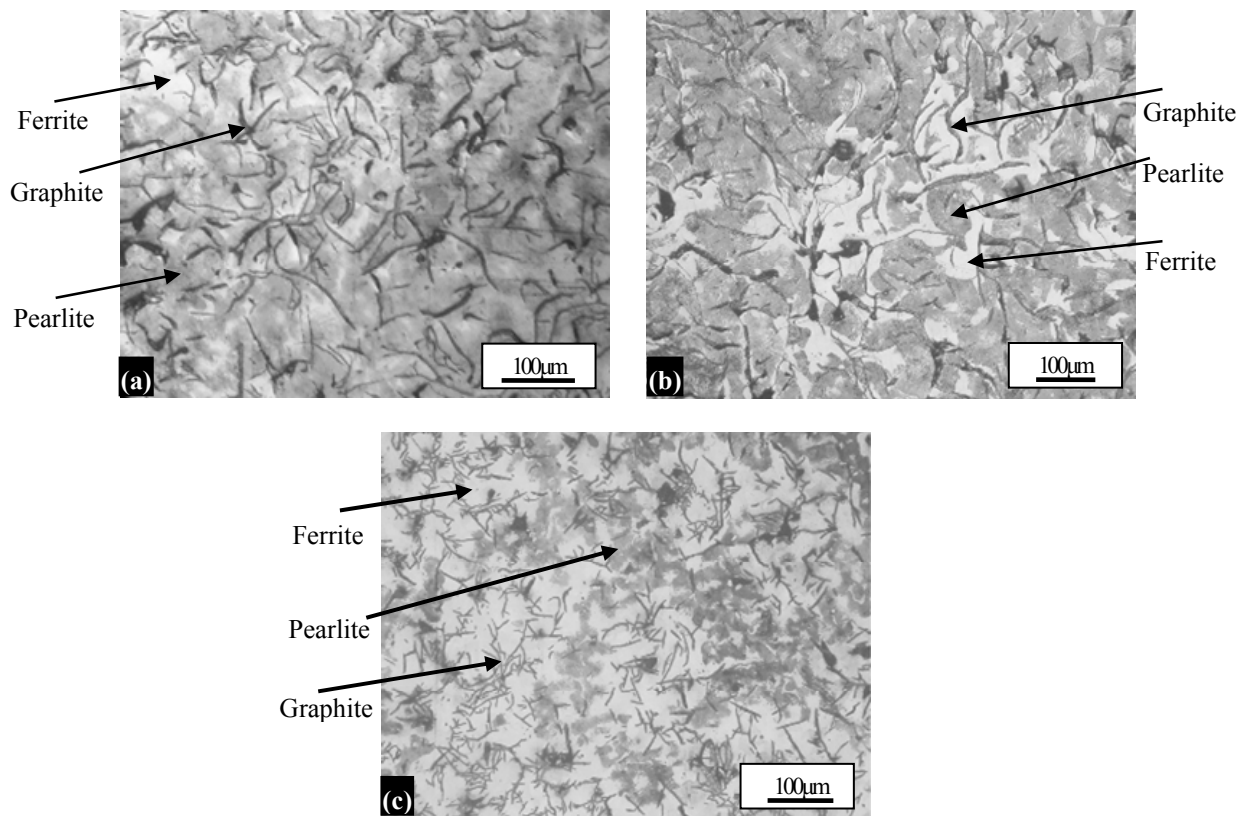


Figure 1. Microstructure of alloyed cast irons with different amounts of Al (a) without aluminium, (b) 2.7% and (c) 4%.

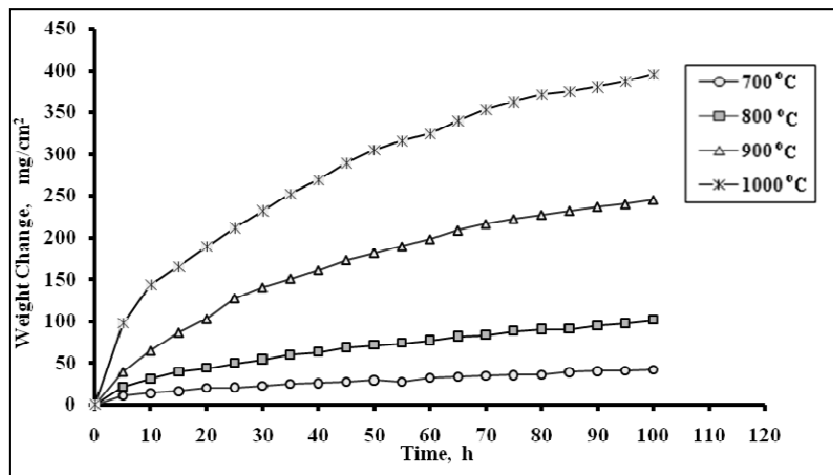


Figure 2. Weight change for aluminum free cast iron (Alloy I) oxidized in air at temperatures 700 - 1000 °C.

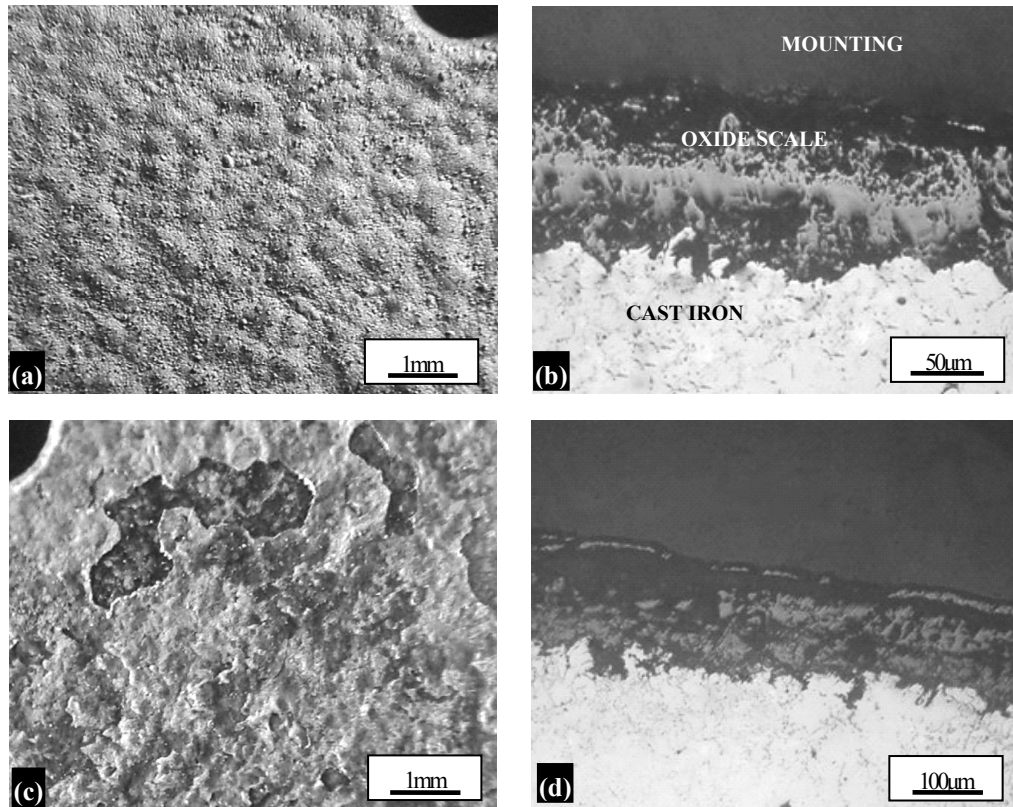


Figure 3. Surface appearance and cross section images of cast Irons (Alloy I) oxidized in air for a period of 100 h at 5 h cycle (a) and (b) 700 °C, (c) and (d) 800 °C.

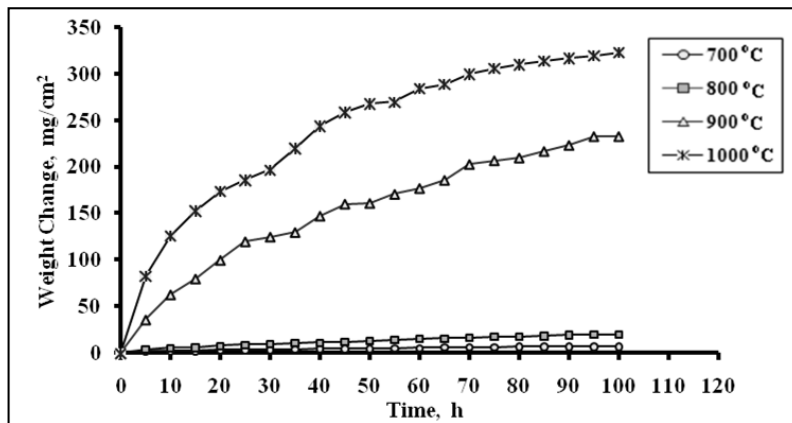


Figure 4. Weight change for cast iron with 2.7 % aluminum (alloy II) oxidized in air at temperatures 700 – 1000 °C.

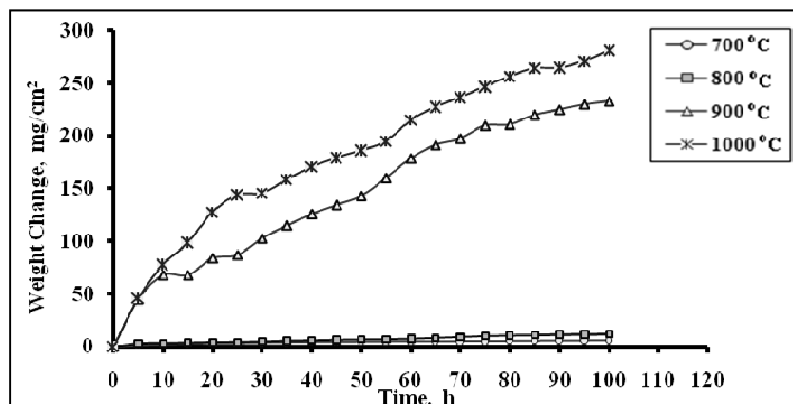


Figure 5. Weight change for cast iron alloyed with 4.0 % Al (Alloy III) oxidized in air at temperatures 700- 1000 °C.

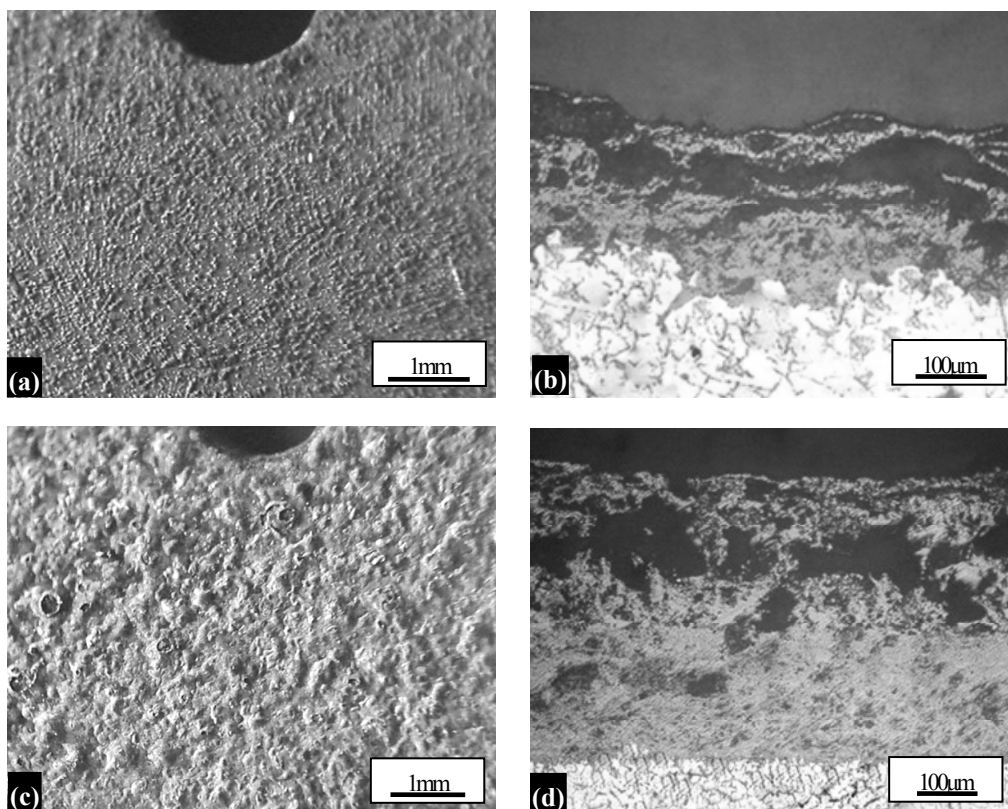


Figure 6. Surface appearance and cross section images of cast Iron (Alloy II) oxidized in air for a period of 5 h (a) and (b) 800 °C, and (c) and (d) 900 °C.