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Oxidation behaviour of Al-alloyed ductile cast irons at elevated temperature

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The oxidation resistance of ductile irons alloyed with aluminium in the range from 0.08 to 6.16 wt.% has been investigated by heating at 550 °C for periods up to 1270 h. Examination by light and SEM microscopy and EPMA indicated that two quite distinguishable layers of oxide were established at the surface. It was found that, in alloys containing aluminium, a very thin and adherent film of aluminium oxide is produced after a short period of heating, which protects the bulk of the alloy from further attack. It is believed that the oxidation resistance can be improved by increasing the aluminium content: an increase in aluminium content led to a decrease in the average thickness of the iron-rich oxide layer. It was also found that the Al addition improved decarburization resistance; after long times at 550 °C a nodular iron with a 6.16% Al content was free of decarburization. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: oxidation resistance; decarburization; ductile cast iron; aluminium; layers of oxide; elevated temperature

INTRODUCTION

Aluminium can be used to control oxidation resistance in cast irons. The effect of aluminium on oxidation resistance is thought to be based on the formation of a very thin, compact and firmly adherent Al-rich oxide film, which gives some protection to the bulk metal from further environmental attack. Previous studies have also shown that having more adherent oxide film obtained by the addition of aluminium can retard the rate of cast iron oxide scale flake-off, and also graphite decomposition. They have suggested that the presence of an Al_2O_3 film on the surface acts as a barrier against the diffusion of oxygen which can decompose the graphite into carbon monoxide (CO) and carbon dioxide (CO_2).[1–6]

EXPERIMENTAL

Oxidation test samples were machined from the as-cast Al containing ductile irons with the composition range given in Table 1 and ground to final approximate dimensions of 25 × 10 × 10 mm. Specimens were placed in small pre-baked crucibles and weighed accurately. Test samples were subsequently exposed at a temperature of 550 °C in an electrically heated muffle furnace for periods up to 1270 h. The specimens were removed from the furnace for different times of exposure and weighed again. At the end of the heating period optical metallographic examination was carried out to measure the depth of penetration below the outermost layer.[7]

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Nikon and Reichert-Jug optical microscopes were used for optical metallography. A Cambridge Series 3 SEM fitted with an Oxford Link ISIS microanalysis system and a Cambridge Series 4 SEM fitted with an Oxford Link ISIS microanalysis system were used for scanning electron microscopy and to study the segregation of Al and Si in the microstructure observed in SEM. An accelerating voltage of 20 kV, a spot size of 2 nm and a working distance of 26 mm were used for the examination.

The XRD analysis was carried out using Cu K_α target radiation. An automated Philips ADP 1700 diffractometer, operated at 40 kV and 20 mA over 2θ values ranging from 5 to 85°, was used in order to detect the reflections of interest.

Microanalysis was performed on samples cut from the as-cast and heat-treated cast irons. After machining and cleaning, samples were mounted in resin blocks that were no more than 15 mm thick, followed by grinding and polishing. A Cameca SX-50 fitted with three wavelength dispersive crystal spectrometers (WDS) and a Link 10/55S solid-state energy dispersive system (EDS) for the detection of characteristic x-rays was used to determine the segregation of silicon and aluminium during solidification and study the homogenization after heat treatment. The EDS is used for rapid qualitative analysis. The crystal spectrometers are used for fully quantitative analyses. The instrument was fully microprocessor controlled, and data acquisition and processing was via a SUN 3/160C workstation. Detection limits for analyses are of the order of 0.1–0.05 element weight % (1000–500 ppm). An electron accelerating voltage of 15 kV and a beam current of 50 nA were selected to analyse the silicon and aluminium distribution between graphite nodules at 1 micron intervals. Pure silicon and pure aluminium were used as reference metals in measurements,

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Table 1. Composition of irons (wt. %)

Alloy	C	Al	Si	Ni	Mn	P	S	Mg	Fe
0.08% Al	3.71	0.08	1.08	0.03	0.09	<0.005	<0.005	0.05	balance
0.48% Al	3.68	0.48	1.06	0.04	0.06	<0.005	<0.005	0.05	″
0.55% Al	3.67	0.55	1.13	0.05	0.06	<0.005	<0.005	0.05	″
0.61% Al	3.66	0.61	1.11	0.04	0.06	<0.005	<0.005	0.04	″
1.71% Al	3.58	1.71	1.18	0.04	0.07	<0.005	<0.005	0.05	″
1.82% Al	3.56	1.82	1.20	0.34	0.09	<0.005	<0.005	0.05	″
2.11% Al	3.55	2.11	1.21	0.04	0.11	<0.005	<0.005	0.06	″
3.10% Al	3.48	3.10	1.24	0.05	0.10	<0.005	<0.005	0.06	″
4.88% Al	3.44	4.88	1.22	0.05	0.10	<0.005	<0.005	0.05	″
6.16% Al	3.25	6.16	1.35	0.07	0.10	<0.005	<0.005	0.06	″

and iron was assumed by difference. In order to map the chemical analyses of the principal alloying elements (Al and Si), an accelerating voltage of 15 kV and a beam current of 50 nA were used on a 512 × 512 pixel array. A beam dwell time of 50 ms was selected for the mapping and a nominal magnification of ×2000. Experimental data correction was provided using Cameca PAP (Pouchou and Pichoir) software.

RESULTS AND DISCUSSION

It was observed that the oxide obtained appeared to be very adherent as no cracking or lifting of the oxide film could be detected, and following the oxidation period the film was not easily removed from the surface.

Optical microscopy and SEM were used to measure the thickness of the oxide layers formed during the oxidation period. It was found that the oxide layers produced on the surface of a number of samples were similar. However, the thickness of the iron oxide layer showed a marked decrease with increasing aluminium content. Al was found to decrease the weight gain during the period of heating (Fig. 1). This behaviour is thought to be caused by the formation of an Al_2O_3 layer.[1,4,5]

Figure 2 plots the variation in oxide penetration values measured for different aluminium contents. It was found that the addition of 6.08% Al decreased the thickness of the outermost oxidation layer by about 40%. This is a reflection of the fact that the oxidation resistance increased with higher aluminium addition.

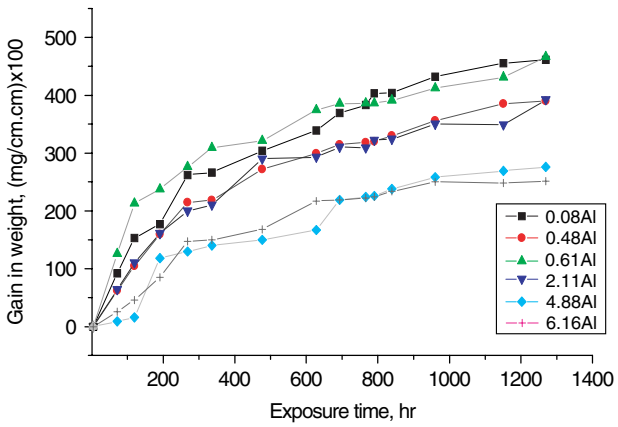

Figure 1. The influence of aluminium on oxidation behaviour (expressed as weight gain) of as-cast ductile irons exposed at 550 °C for different times.

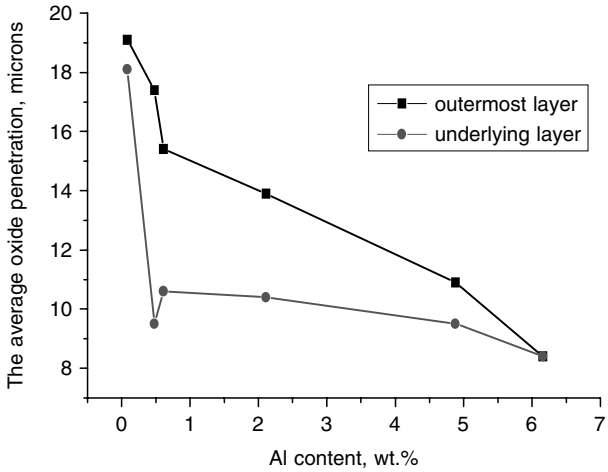

Figure 2. Oxidation behaviour of Al alloyed spheroidal iron at 550 °C for 1270 h.

An electron probe microanalysis (EPMA) examination indicated that the layers are not completely homogeneous as the distribution of the alloying elements shows changes both across and along the thickness (Figs 3 and 4).

The element mapping shows that after the long holding period at 550 °C the graphite nodule very close to the surface has been removed by decarburization (Fig. 3). On the other hand, as shown in Fig. 4, the iron map indicates that for a higher level of aluminium addition, the graphite nodule very close to the surface shows no clear changes during the oxidation period. It seems that the 6.16% Al concentration in the iron reduced the decarburization tendency as compared with 0.48% Al.

CONCLUSIONS

An oxide rich in iron is produced during the initial time period, before a complete and adherent film of aluminium oxide forms. It is believed that the formation of an aluminium oxide layer acts as a diffusion control process, to reduce the rate of iron oxidation.

As the amount of aluminium increases, the protective Al-rich layer can be formed at a shorter time and result in

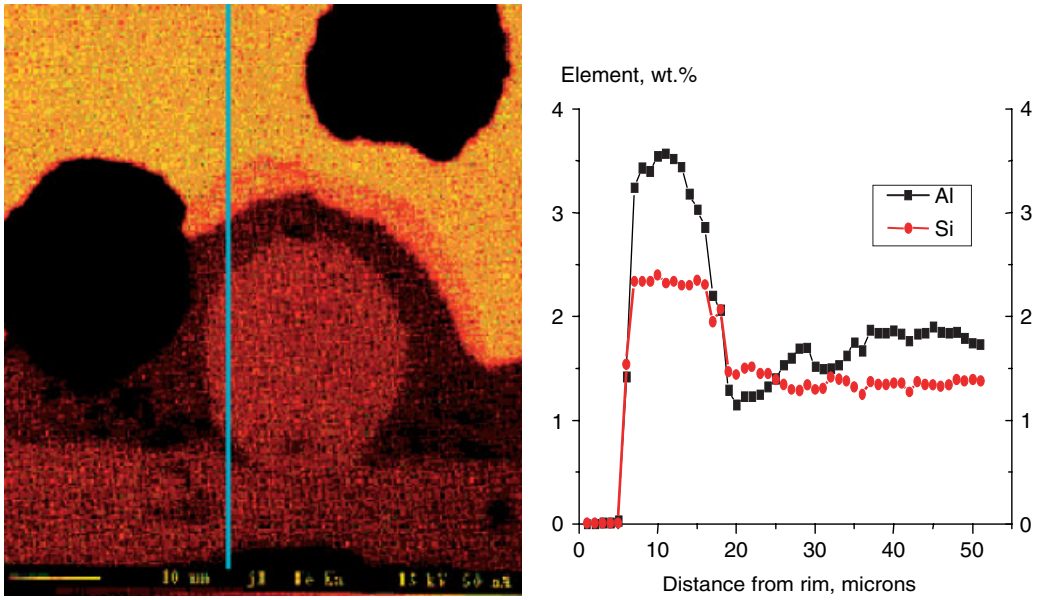

Figure 3. Distribution map of iron, aluminium and silicon over the adherent oxides established on the 0.48% Al ductile iron held at 550 °C for 1270 h; (a) iron map and (b) the corresponding line traverse of aluminium and silicon across the thickness of the oxide layers.

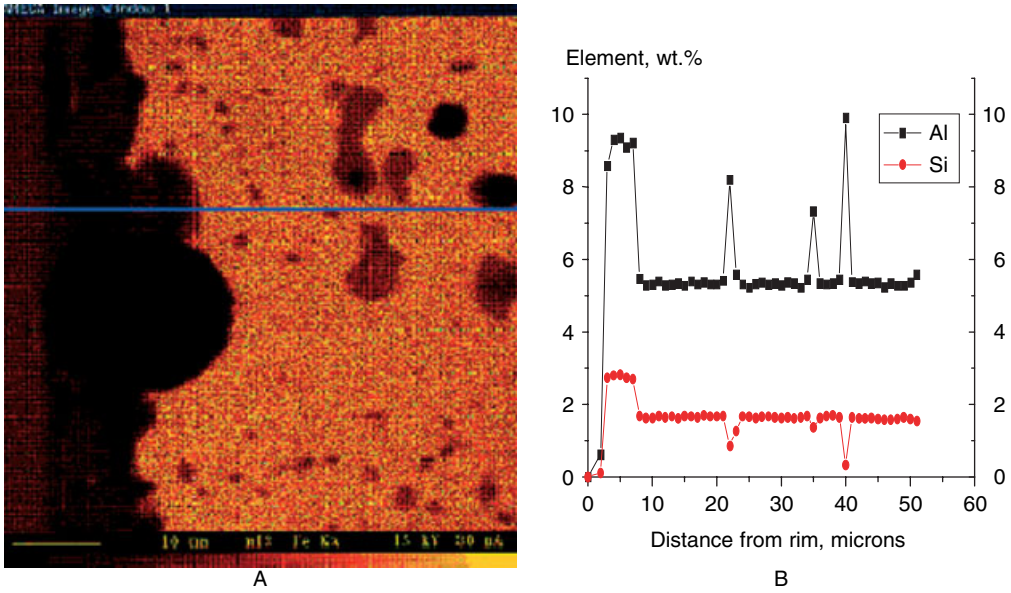

Figure 4. Distribution map of iron, aluminium and silicon over the adherent oxides established on the 6.16% Al ductile iron held at 550 °C for 1270 h; (a) iron map and (b) the corresponding line traverse of aluminium and silicon across the thickness of the oxide layers.

lower oxidation and decarburization rates, for a higher level of Al addition.

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