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Thermally induced surface changes in aluminium–iron oxide thermites

PU SEN WANG
Monsanto Research Corporation, Mound, Miamisburg, Ohio 45342 USA*

The aluminium and iron oxide surfaces of Al–Fe_3O_4 thermite in powder and pressed pellet form were studied before and after accelerated ageing at 180° C by X-ray photoelectron spectroscopy. The Al_2O_3 surface film thicknesses on aluminium metal were deduced from the intensity ratio of aluminium K L L Auger signals induced by X-ray radiation on Al_2O_3 and aluminium metal. Based on the mean free path of 1.65 nm for aluminium K L L Auger electrons, the oxide thickness on aluminium flakes before mixing with Fe_3O_4 was estimated to be 0.8 to 0.9 nm. A slight oxidation was observed on the aluminium surface after mixing with Fe_3O_4 at room temperature. Hot pressing of this mixture at 425° C for 7 min increased the oxide film to 3.1 nm. This surface oxide film seemed to protect the aluminium metal, and further ageing at 180° C did not cause significant oxide growth.

1. Introduction

Thermites are a valuable heat source. Previously, X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) had been used to analyze the Al–Cu_2O system [1, 2]. We have reported the Al_2O_3 film thicknesses on aluminium metal surfaces increased during mixing with Cu_2O, ageing at 180° C, and pelletizing at 425° C of Al–Cu_2O thermite. However, the thick oxide film induced by pelletizing proved to protect aluminium fuels in the thermites, and further ageing at 180° C caused no change in the surface oxide films [1]. This is believed to be important to material compatibility. By Auger sputtering technique, we observed a mixed zone of aluminium and Cu_2O of at least 10.0 nm caused by the pelletization [2]. This mixed zone is believed to be critical to the ignition mechanism of thermite.

For certain applications, a higher heat output than that afforded by the Al + Cu_2O reaction (2.427 kJ g^{-1}) is desirable. Therefore, we developed an Al–Fe_3O_4 thermite as a chemical heat source. In the reaction

$$8\,Al + 3\,Fe_3O_4 \rightarrow 4\,Al_2O_3 + 9\,Fe,$$

3.682 kJ are theoretically produced by each gram of the reactants when mixed stoichiometrically. As before, we were interested in the ignitability and lifetime expectancy of such composites after consolidation. It is apparent that contact between the reactant particles at the elevated temperatures used in the powder consolidation process may alter the constituency of the pellets. Therefore, the surfaces of the aluminium both before and after consolidation, as well as after accelerated ageing, were characterized. These results are reported.

2. Experimental procedures and techniques

Alcoa aluminium flakes and Cerac "pure" Fe_3O_4 were mixed in a V-blender for 1 h at room temperature to form a theoretically stoichiometric thermite composition. The pellets (6 mm diameter × 2 mm height) were hot pressed at 425° C in a nitrogen environment for 7 min under 12 000 psi in a preheated graphite die. Accelerated ageing was accomplished by heating samples at 180° C in glass containers open to air.

The spectrometer used in this study was a modified AEI ES-100 XPS spectrometer with Bremsstrahlung radiation of a magnesium anode. Pressure in the sample chamber was reduced to 10^{-8} torr with the aid of two 250 litre sec^{-1}

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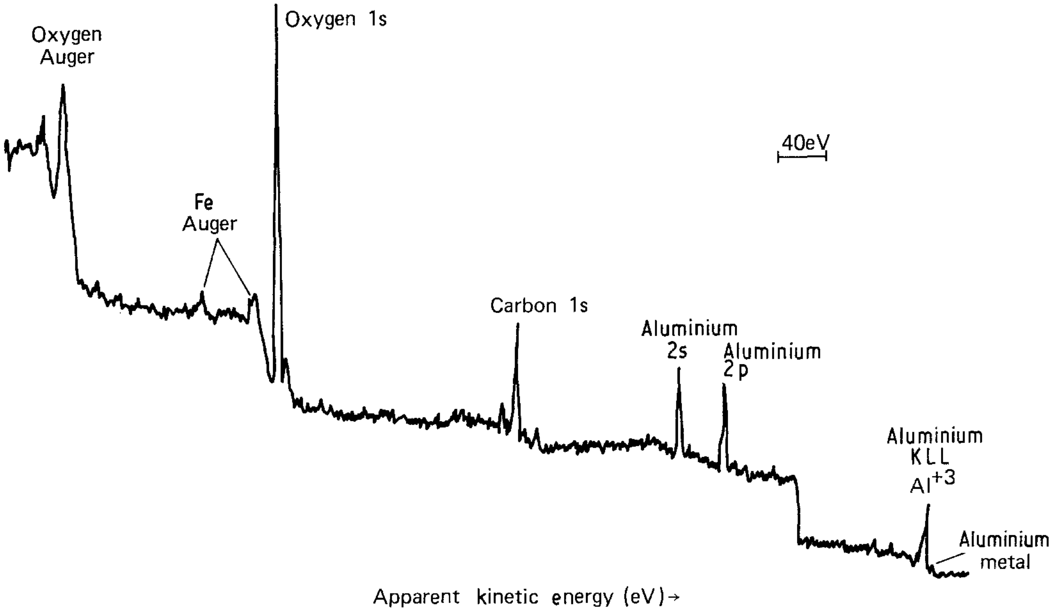

Figure 1 X-ray photoelectron spectrum of an Al–Fe_3O_4 pellet pressed at 425° C and aged at 180° C for 24 days in open air, irradiated by Bremsstrahlung.

diffusion pumps and one 260 litre sec^{-1} turbomolecular pump [1, 3].

3. Results and discussion

3.1. Oxide thickness calculation and overall surface XPS scan

An example of the overall XPS scan of a typical, consolidated Al–Fe_3O_4 thermite sample is shown in Fig. 1. This sample was a hot-pressed pellet aged at 180° C for 24 days. The XPS signals of oxygen 1s, carbon 1s, aluminium 2s, and aluminium 2p are clearly identified. At the lower kinetic energy side of the spectrum, the Auger electron signals due to oxygen and iron can also be observed. The most well-resolved signals are those associated with the aluminium K L L Auger for Al_2O_3 and aluminium metal; these signals appear at the higher kinetic energy side of the spectrum.

The equation to calculate the oxide film thicknesses on the aluminium surfaces is [1, 4]:

$$d_0 = \lambda_0 \ln \{(I_0/I_m)(I_m^\infty/I_0^\infty) + 1\} \qquad (1)$$

where λ_0 is the mean free path of an Al_2O_3 electron; I_0, I_m are the measured spectroscopic signal intensities for Al_2O_3 and aluminium metal, respectively, for our samples; and I_0^∞ and I_m^∞ are intensities for "infinitely" thick samples of such materials. Battye *et al.* [5] obtained a value of 1.65 nm for λ_0 for the aluminium K L L Auger electron from Al_2O_3 (kinetic energy 1385 eV). The ratio I_m^∞/I_0^∞ was experimentally determined to be 0.751 using specially prepared aluminium and Al_2O_3 samples. The oxide film thickness, d_0, on aluminium could, therefore, be calculated from the equation.

A comparison of aluminium powder spectra before and after ageing is shown in Fig. 2. Spectra in Fig. 2a show the aluminium 2p signals of Al_2O_3 and aluminium metal at 119.4 eV and 116.9 eV, respectively. It is obvious from the spectra shown in Fig. 2c that Al_2O_3 increased and aluminium metal decreased after the aluminium powder aged for 68 days at 180° C. The same conclusions can be drawn from an evaluation of the changing ratio of aluminium 2s signals for Al_2O_3 and aluminium metal at 74.1 eV and 71.1 eV, respectively; such changes are seen in Figs. 2b and d. Neither the aluminium 2p nor the aluminium 2s signal was resolved well enough to permit unambiguous deconvolution; therefore, surface oxide film thickness calculations were based on aluminium K L L Auger signals. The high resolution aluminium K L L signals induced by X-ray irradiation on this aluminium powder surface are shown in Fig. 3. A 7.5 eV difference in kinetic energy was observed between Al_2O_3 and aluminium metal. The signal intensity ratio Al_2O_3/aluminium metal was 47/53 for the powder received from the manufacturer. Using 1.65 nm as the λ_0 value and 0.751 for (I_m^∞/I_0^∞), we calculated the oxide film thickness, d_0, for this sample to be 0.84 nm. This agrees well

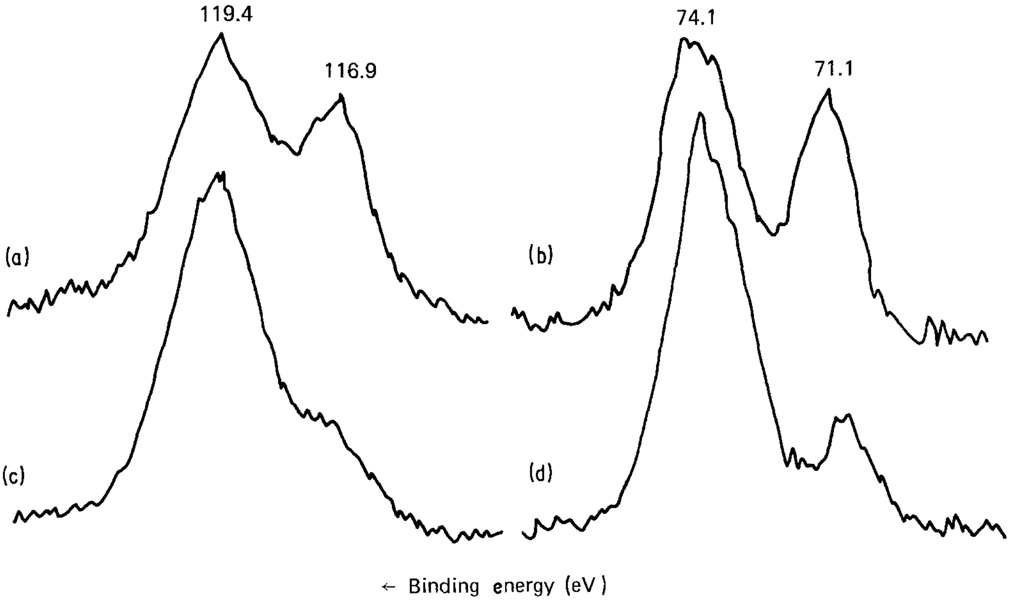

Figure 2 (a) Aluminium 2p and (b) aluminium 2s XPS from aluminium powders stored at room temperature; (c) and (d) are the same signals from the powders stored for 68 days at 180° C.

with the previous value of 0.87 nm obtained using a silicon anode with similar aluminium powders in the Al–Cu_2O studies already cited [1]. Ageing this powder at 180° C for 68 days in open air changed the Al_2O_3/aluminium metal signal intensity ratio (normalized to exclude the plasmon signal) to 74.5/24.5; the surface oxide thickness is now 1.92 nm using this intensity ratio. Thus, a considerable growth of the oxide layer occurred during this accelerated ageing period. Oxide thickness data for aluminium powders aged for different periods of time at 180° C are tabulated in Table I; a plot of these data together with oxide growth in Al–Fe_3O_4 compositions is shown in Fig. 4.

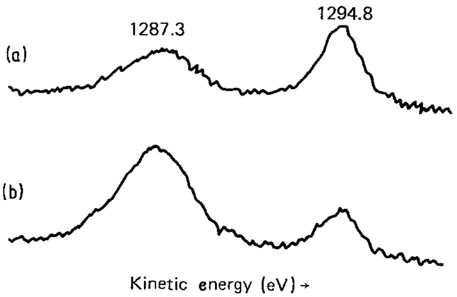

Figure 3 X-ray induced aluminium K L L Auger spectra of (a) aluminium powders stored at room temperature and (b) aged 68 days at 180° C.

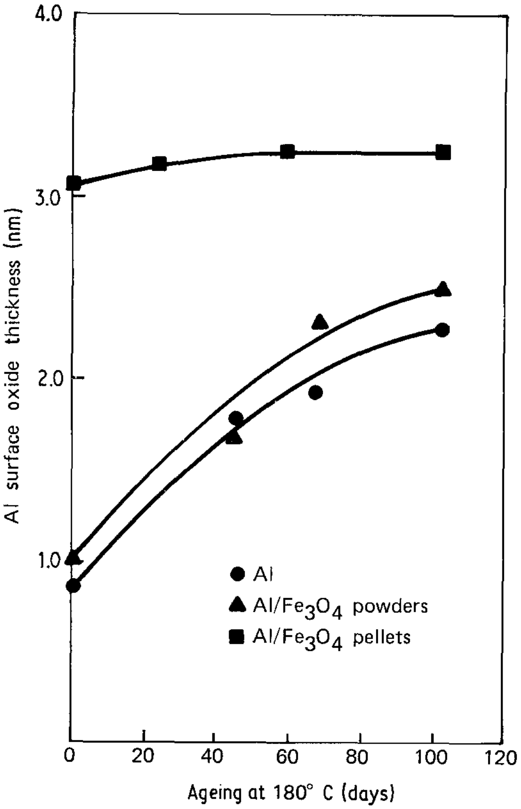

Figure 4 Aluminium oxide layer growth during ageing at 180° C in open air.

TABLE I Aluminium K L L AES data for aluminium powders showing effects of thermal ageing

Ageing Condition	Signal	Apparent kinetic energy (eV)	Signal area (%)	Oxide thickness (nm)
Aluminium powder stored at room temperature	Plasmon	–	–	–
	Oxide	1287.1	47.0	–
	Metal	1294.3	53.0	0.84
45 days at 180° C	Plasmon	–	–	–
	Oxide	1286.5	72.0	–
	Metal	1293.8	28.0	1.77
68 days at 180° C	Plasmon	1278.8	7.5	–
	Oxide	1287.3	69.0	–
	Metal	1294.8	23.5	1.92
103 days at 180° C	Plasmon	1278.4	5.5	–
	Oxide	1287.2	75.5	–
	Metal	1294.7	19.0	2.28

3.2. Aluminium powder surface analysis

In order to determine changes to aluminium caused by processing and storage with Fe_3O_4, it was necessary to characterize the surface of the aluminium powder itself. Representative XPS scans of oxygen 1s and carbon 1s for such aluminium powder surfaces before and after accelerated ageing at 180° C are presented in Fig. 5. As expected, an oxygen 1s signal attributed to Al_2O_3 was detected at a binding energy of 532.1 eV, as shown in Fig. 5a, on the aluminium powder received from the maufacturer. The fact that this signal grew larger after thermal ageing, as seen in Fig. 5c, suggests that oxygen continues to diffuse into the aluminium metal. As seen in Fig. 5b, carbon 1s signal was observed at binding energies of 285.0 eV. This signal is due to the hydrocarbon. After thermal ageing, intensity of this signal was significantly reduced. This result agreed with previous studies [1] of the Al–Cu_2O thermite where a silicon anode was employed.

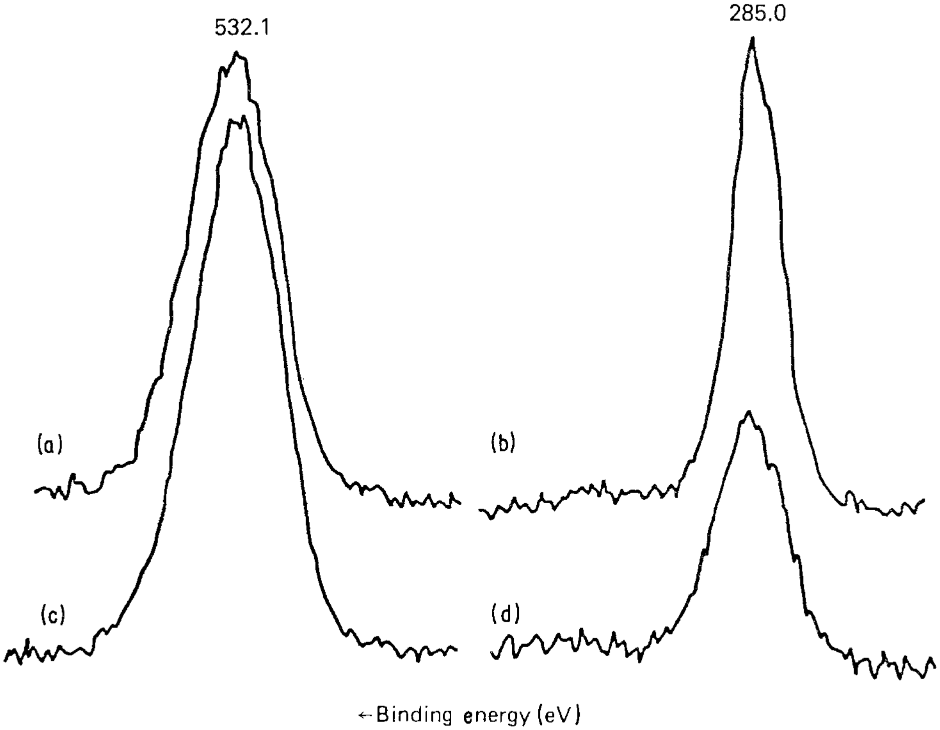

Figure 5 (a) Oxygen 1s and (b) carbon 1s XPS signals of aluminium powders stored at room temperature; (c) and (d) are the same signals from the powders stored for 68 days at 180° C.

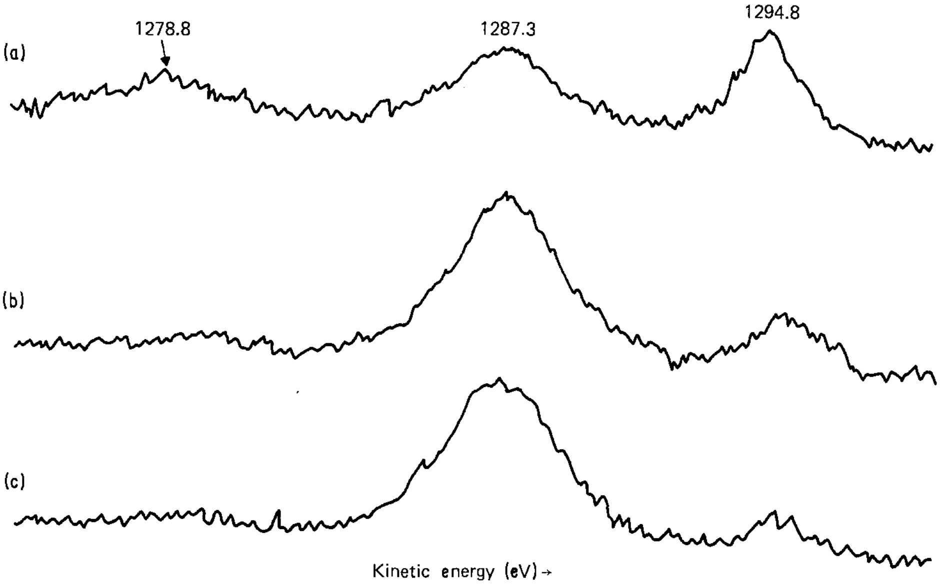

Figure 6 Aluminium K L L Auger spectra of Al–Fe_3O_4 sample; (a) stored at room temperature, (b) stored at 180° C for 68 days, and (c) pelletized at 425° C for 7 min.

3.3. Surface analysis of Al–Fe_3O_4 thermite

The characteristic signals from the aluminium powders in the mixture are similar to those from aluminium alone. However, the oxide to metal K L L signal intensity ratio increased from 0.887 to 1.09 (see Fig. 6) as a result of mixing with Fe_3O_4. Dry mixing at room temperature of aluminium powder with iron oxide powder to form the thermite composite apparently caused a significant amount of oxidation of the aluminium surface. Oxide film thickness increased by 18% from 0.84 nm to 0.99 nm. A similar behaviour was observed in the Al–Cu_2O studies [1]. Subsequent ageing of the thermite powders caused further growth of the oxide layer as seen in Table II and Fig. 4. A comparison of the data in Tables I and II and the corresponding plots in Fig. 4 indicates that the oxide growth rate on aluminium in the thermite composite is about the same as that on aluminium powder heated alone in air. Oxidation of aluminium powder surfaces is therefore caused by atmospheric oxygen rather than Fe_3O_4 at 180° C; this is understandable in view of the limited surface contact between aluminium and Fe_3O_4 in the loose powders. Hot pressing of this thermite powder at 425° C for 7 min under nitrogen caused substantial oxidation of the aluminium surface and increased the oxide layer to 3.06 nm as seen in Fig. 6c.

TABLE II Aluminium K L L AES data for Al–Fe_3O_4 thermite powders showing effects of thermal ageing

Ageing condition	Signal	Apparent kinetic energy (eV)	Signal area (%)	Oxide thickness (nm)
Al–Fe_3O_4 powder stored at room temperature	Plasmon	1281.0	17.5	–
	Oxide	1290.0	43.0	–
	Metal	1297.0	39.5	0.99
45 days at 180° C	Plasmon	1281.2	9.5	–
	Oxide	1289.2	63.5	–
	Metal	1296.8	27.0	1.68
68 days at 180° C	Plasmon	1281.2	6.5	–
	Oxide	1289.1	75.0	–
	Metal	1296.1	16.5	2.30
103 days at 180° C	Plasmon	1281.1	6.0	–
	Oxide	1290.0	77.5	–
	Metal	1297.4	16.5	2.49

TABLE III Aluminium K L L AES data for Al–Fe_3O_4 thermite pellets showing effects of thermal ageing

Ageing condition	Signal	Apparent kinetic energy (eV)	Signal Area (%)	Oxide thickness (nm)
Al–Fe_3O_4 pellet at room temperature	Plasmon	1281.8	5.5	–
	Oxide	1290.0	83.0	–
	Metal	1297.4	11.5	3.06
24 days at 180° C	Plasmon	1281.2	4.0	–
	Oxide	1289.7	85.0	–
	Metal	1297.3	11.0	3.16
59 days at 180° C	Plasmon	1281.2	3.5	–
	Oxide	1289.4	86.0	–
	Metal	1296.7	10.5	3.25
103 days at 180° C	Plasmon	1279.5	3.3	–
	Oxide	1287.8	86.4	–
	Metal	1295.4	10.3	3.26

Further ageing at 180° C caused only a slight further increase in the oxide layer. These data are tabulated in Table III and plotted in Fig. 4.

One pellet was split open to characterize the inner surface; the inner surface oxide layer was found to be thinner than that of the outer surface.

4. Conclusion

Thermal induced aluminium oxide film changes can be measured from aluminium 2p and aluminium 2s XPS signal intensities during blending and accelerated ageing of Al–Fe_3O_4 thermites. The aluminium K L L Auger signals induced by X-ray radiation of aluminium fuel give an accurate oxide thickness measurement. Based on the mean free path of 1.65 nm for aluminium K L L Auger electrons, the oxide thickness on aluminium flakes before mixing with Fe_3O_4 was estimated to be 0.8 to 0.9 nm. A slight oxidation was observed on the aluminium surface after mixing with Fe_3O_4 at room temperature. Hot pressing of this mixture at 425° C for 7 min increased the oxide film to 3.1 nm. This surface oxide film seemed to protect the aluminium metal, and further ageing at 180° C did not cause significant oxide growth.

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