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Al/Cu_2O THERMITE COMPATIBILITY STUDIES BY X-RAY PHOTOELECTRON AND X-RAY INDUCED AUGER SPECTROSCOPY

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ABSTRACT

The surface chemistry of Al/Cu_2O thermite in powdered mixtures and in pressed pellets was studied before and after accelerated agings with x-ray photoelectron spectroscopy (XPS) and with x-ray induced Auger spectroscopy (XAES). The kinetic energies of the XPS or XAES signals were observed for Al 1s, Cu $2p_{1/2}$, Cu $2p_{3/2}$, Cu L_3-MM, O 1s, Al K-LL, C 1s and Cu 3s.

The Al_2O_3 film thicknesses on Al metal surfaces were deduced from signal intensity ratios of Al^{+3} and Al in XPS of Al 2s and from Al K-LL XAES signals. The oxide thicknesses on Al powders from the manufacturer were measured. Mixing Al with Cu_2O at room temperature, to form the thermitic composition, induced oxidation of the Al and increased the oxide film thickness. Hot pressing of thermite powders at 425°C to form pellets was found to double the oxide layer. This oxide layer was found to protect the Al fuel; further aging of these pellets at 180°C for several months showed a negligible change in composition and thickness of the surface oxide. The bulk of the pellet was found to be stable and of good quality.

Stearic acid, the organic additive to Al powders, was detected by the C 1s signal. The CuO impurity in Cu_2O was observed in the Cu $2p_{3/2}$ signal which was broadened by unpaired electron spin-spin interaction in the Cu^{+2} d^9 orbital; both impurities were removed during the high temperature pressing operation.

INTRODUCTION

The Al/Cu_2O thermite is a valuable chemical heat source because 580 cal of heat is released for each gram of Al/Cu_2O mixture according to the reaction:

$$2Al + 3Cu_2O \rightarrow Al_2O_3 + 6Cu. \qquad (1)$$

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Aluminum powder, being very sensitive to oxygen or other oxidizers, immediately grows a film of Al_2O_3 on its surface after exposure to the air. This oxide film may or may not protect the aluminum metal inside (which is our thermite fuel) under various fabrication and storage conditions. If the layer grows too thick, in addition to the problem of losing too much of the fuel and thus lowering the heat output, compatibility problems can be anticipated because of the fact that Al_2O_3 has a much higher melting point (2050°C compared to 660°C for aluminum metal). Consequently, the thickness of the oxide film on the aluminum surface during the stages of production, fabrication, and storage is indeed critical to the material quality and compatibility.

To increase the energy output per unit volume, thermite powders need to be pressed to pellets of various desired shapes for special use. Therefore, it is necessary to heat the powders to 425°C or above, depending on the size and geometry to be consolidated. This heating process inevitably promotes a certain degree of oxidation in aluminum metal. We are concerned with the degree of influence this heating has on the quality of the thermite. Stearic acid has been added to aluminum powders by the manufacturer as a lubricant and surface protector; the role played by this "impurity" in our thermite may also be informative.

The main interest of this study is to measure the thicknesses of aluminum oxide layers on aluminum particles during production, fabrication, and storage by x-ray photoelectron spectroscopy (XPS), or electron spectroscopy for chemical analysis (ESCA), and X-ray induced Auger electron spectroscopy (XAES). (ref. 1, 2)

EXPERIMENTAL

Sample preparation and aging

Theoretically stoichiometric thermite mixtures (11 wt % Al and 89 wt % Cu_2O) were produced by dry mixing Reynolds XD28 aluminum flakes and Cerac "pure" cuprous oxide in a V-Blender for 1 hr (ref. 3). Aluminum flakes were used as received and Cu_2O powders were sieved through a 400-mesh screen to remove oversized particles. Thermite pellets about 6 mm in diameter, about 2 mm in height, and at 90% of theoretical density were pressed from powders with preheated graphite dies under dry nitrogen at 425°C and 12,000 psi for 15 min (ref. 3,4).

Thermite mixtures, thermite pellets, and aluminum powders were sealed into glass tubes separately. Two environments were used: dry air and argon. Samples were aged at desired temperatures for desired periods.

Spectrometer

The XPS spectrometer is a modified AEI ES-100 instrument. This spectrometer with the accompanying argon ion sputtering capability has been discussed in more detail elsewhere (ref. 5). The system is pumped by two 250-liter/sec turbomolecular pumps, the vacuum achievable in the sample chamber being 10^{-8} torr. The chamber

reaches baking temperatures of more than 150°C. Reactive vapors can be minimized in the system by baking, by using a titanium sublimation pump, and by two liquid nitrogen cryostations. The anode used for all the XPS measurements was silicon.

RESULTS AND DISCUSSION

Calculation of surface oxide and carbon film thicknesses

The oxide thickness (d_o) on aluminum particle surfaces can be calculated from the following equation: (ref. 6-8):

$$d_o = \lambda_o \ln \{(I_o/I_m)(I_m^\infty/I_o^\infty) + 1\} \quad (2)$$

where λ_o is the mean free path of an Al_2O_3 electron. I_o, I_m are measured spectroscopic signal intensities for Al_2O_3 and Al metal, respectively, for our samples. I_o^∞ and I_m^∞ are intensities for "infinitely" thick samples of such materials. The carbon film thickness (d_c) can be calculated from (ref. 7, 8):

$$d_c = - \lambda_c \ln \{1 - \frac{I_c}{I_c^\infty}\} \quad (3)$$

where λ_c is the mean free path of an electron from carbon, and I_c and I_c^∞ are the carbon signal intensities of the thermite sample and of the sample of "infinite" carbon thickness, respectively.

The mean free path of a photoelectron is dependent on its kinetic energy and the material through which it passes. Battye et al. (ref. 9) have studied the attenuation of the photoelectron from Al_2O_3 (kinetic energy from 157 to 1404 eV). A least-squares fit model which has been developed was used to extend the data over 1600 eV to cover our kinetic energy range and our mean free path of Al_2O_3 was extrapolated from the curve (ref. 10). A λ_o of 16.5 Å was obtained for Al KLL Auger with 1385 eV kinetic energy and 18.1 Å for Al 2s ESCA at 1615 eV kinetic energy.

To evaluate λ_c through a carbon layer, Wagner has shown that the relation between λ_c of a photoelectron to its kinetic energy E is:

$$\lambda_c = KE^p \quad (4)$$

where K and p are constants (ref. 11). Henke has shown that the attenuation lengths in stearic acid multilayers are 60 Å and 90 Å for 750 eV and 1350 eV, respectively (ref. 12). This gives K = 0.62365 and p = 0.68983 and

$$\lambda_c = 0.62365E^{0.68983} \quad (5)$$

λ_c was found to be 94.7 Å for C 1s ESCA electrons.

To measure I_c^∞ (the total intensity of an infinitely thick carbon layer) high-molecular-weight carbon-containing compounds such as candle wax, Apiezon grease, and stearic acid were layered on a 5-mm x 5-mm aluminum foil for measurements. Proof of "infinite" thickness of the carbon layer was obtained by scanning the KLL Auger aluminum lines without observing the signal. An averaged value of 890 counts-eV/sec was obtained from these measurements.

To measure the signals of an aluminum oxide layer of infinite thickness (I_o^∞) several layers of 5-mm x 5-mm aluminum foils were aged at 400°C for 12 hr to convert the surfaces completely to aluminum oxide, which was proved by the absence of any metal signals. Values of 5725 and 573 counts-eV/sec were obtained for Al KLL Auger and Al 2s ESCA, respectively.

The total intensity of an "infinitely" thick Al metal sample (I_m^∞) was obtained by measuring a fresh Al surface cleaned by argon ion-etching. An oxide build-up curve was established in Al 1s ESCA to calibrate possible surface oxide growth during the measurements. The values of I_m^∞ are 4298 and 501 counts-eV/sec for KLL Auger and Al 2s ESCA, respectively.

Surface analysis of aluminum powders

It is logical to study the surface structures of aluminum powders alone as background knowledge for further study of thermite mixtures. Fig. 1 gives the overall ESCA spectra of (a) aluminum flakes aged at 180°C and (b) thermite powders aged at 180°C; both samples were irradiated by Si K_α under the same spectrometric conditions.

Carbon 1s signal - stearic acid in aluminum powders. This carbon photopeak could be deconvoluted into a doublet structure, which is characteristic of carbon present in more than one chemical form. The two peaks noted can be attributed to carbon of a straight-chain hydrocarbon and carbon of a carboxylate species (Fig. 2a). The ratio of the straight-chain hydrocarbon at 284.8 eV to the carboxylate carbon at 286.6 eV was 14:1. By comparing this signal (carbon 1s photopeak) with the signal of the specially prepared standard stearic acid sample (Fig. 2b), it was subsequently identified to be from the stearic acid $\{CH_3(CH_2)_{16}CO_2H\}$ added to the aluminum powders by the manufacturer. The theoretical ratio of the two peaks should be 17:1.

The amount of stearic acid was found to be less at the higher storage temperature, as expected, because of removal by higher vapor pressure at the higher temperature. Fig. 2c shows that only 75% of the stearic acid remains in the sample after aging at 180°C in dry air for 40 days. The amount of carbon measured at the higher storage temperature in argon was found, in general, to be less than the amount of carbon measured at the same temperature for storage in dry air.

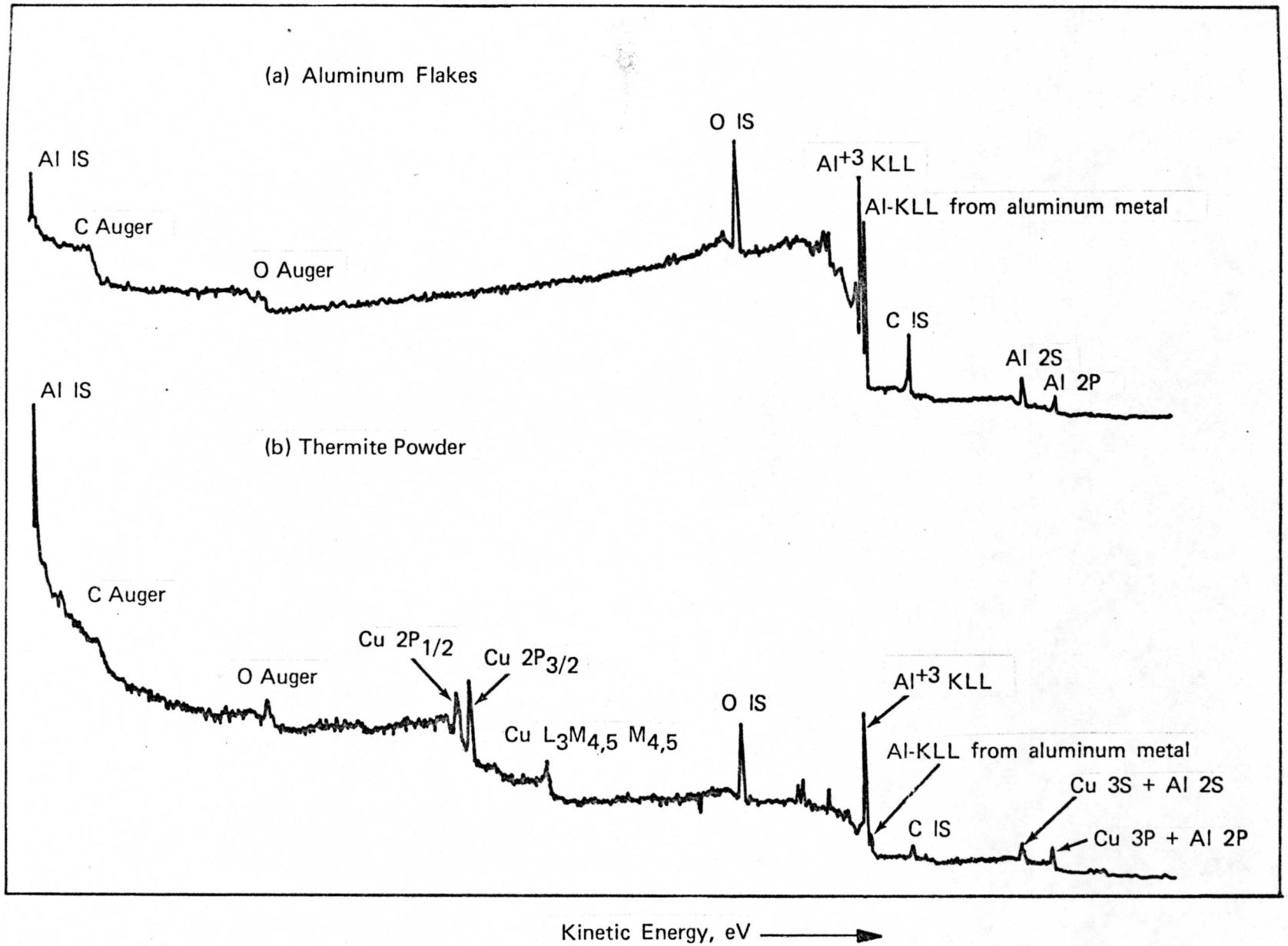

Fig. 1. Overall XPS spectra of (a) 180°C aged flaked aluminum and (b) 180°C aged thermite powder specimens. Both spectra were excited by SiK_{α} radiation.

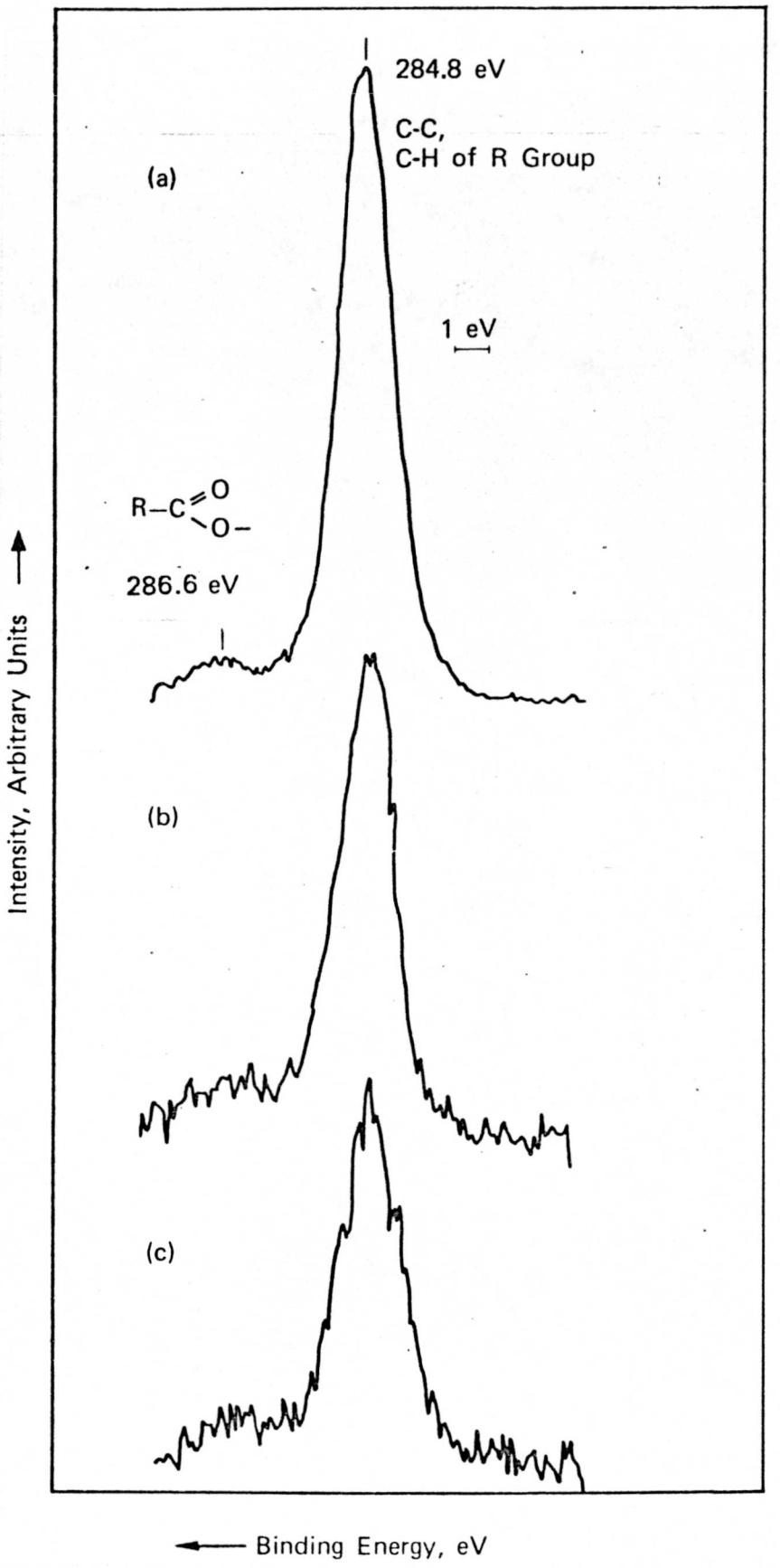

Fig. 2. ESCA carbon 1s photopeak of stearic acid in: (a) aluminum flakes stored at room temperature, (b) stearic acid sample, and (c) aluminum powder stored at 180°C for 40 days in dry air.

Surface change in aluminum powders alone. The carbon layer on the aluminum powder before aging is approximately 50-60 Å thick because of added stearic acid and tended to be destroyed by aging. Residual carbon after aging could be attributed to the x-ray tube or the atmosphere. Fig. 3 shows such a change in the carbon 1s signal intensity during aging. Table 1 gives results of layer thicknesses during this period from Al KLL Auger and Al 2s ESCA data. Fig. 4 shows aluminum KLL Auger of powder stored at room temperature, powder stored at 180°C for 40 days, powder stored at 180°C for 91 days, and flamed foil. Fig. 5 shows the 2s photoelectron peaks for the same samples. The thicknesses of these oxide layers are also shown in Table 1.

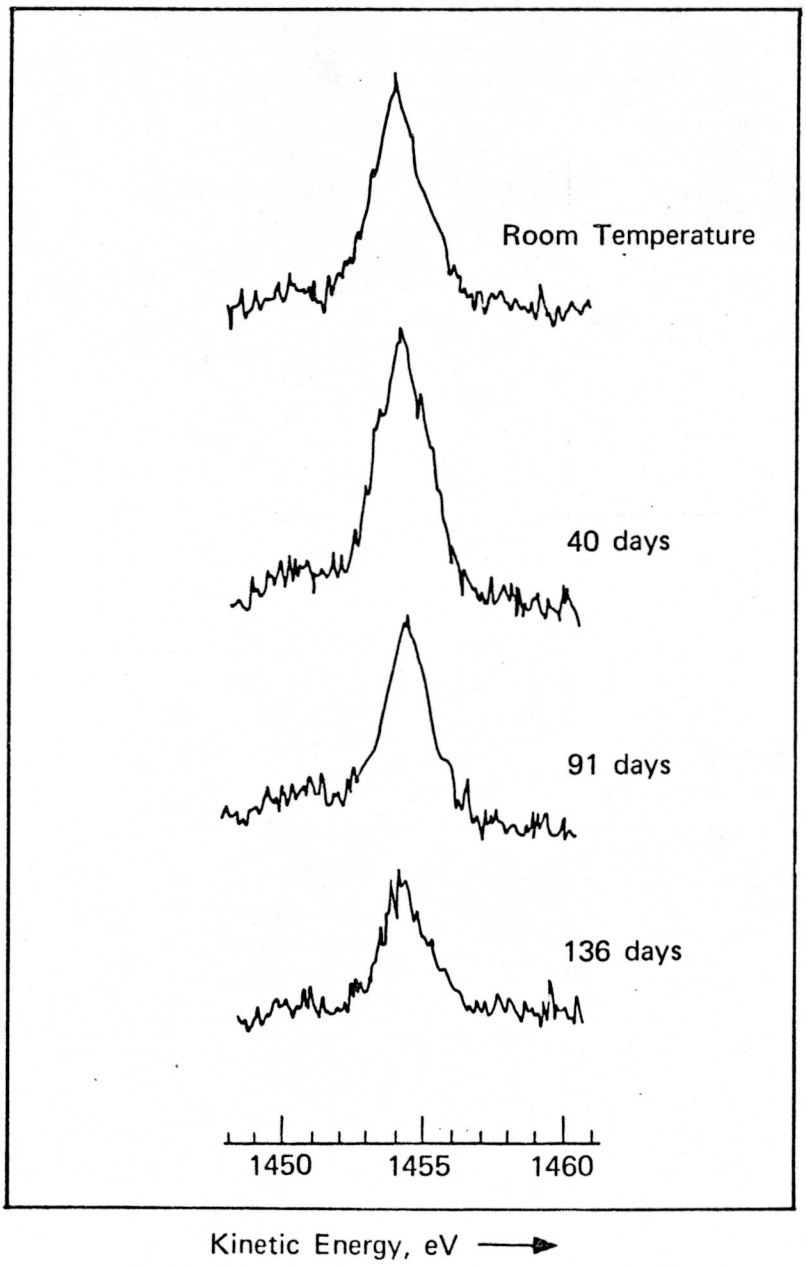

Fig. 3. Carbon 1s XPS of aluminum powders aged at 180°C in air for various periods.

TABLE 1

Aluminum-KLL Auger and 2s ESCA results for aluminum powders aged in different environments

Sample	d_c (Å)	d_o (Å)	
		KLL Auger	Al 2s
Aluminum powder in air at room temperature	64.4	8.7	11.1
Aluminum powder in air 40 days at 180°C	56.8	11.6	12.4
Aluminum powder in air 91 days at 180°C	62.3	13.0	13.0
Aluminum powder in air 136 days at 180°C	41.8	13.0	14.0
Aluminum powder in argon 40 days at 180°C	---	10.6	9.1	11.2
Aluminum powder in argon 91 days at 180°C	16.9	9.1	10.8
Aluminum powder in argon 136 days at 180°C	26.7	12.0	12.0

Aluminum powders from the manufacturer have an oxide layer of about 9 Å as expected because of exposure to the air during storage. This layer increased to about 12 Å when aged about 40 days in air at 180°C and to 13 Å in 3 mo. After 3 mo there seems to be no further increase, possibly because of the small size of the sample tube (which could not supply additional air). As expected, since no oxygen was present, storage under argon at 180°C for 40 and 91 days showed no increase in the oxide layer (about 9 Å), but the result for 136 days could be an experimental error. The results derived from Al 2s ESCA are slightly higher than those from the Auger process but show the same trend. The deviation of results from KLL to 2s can be attributed to two reasons:

(1) The 2s signals are not well resolved; there is a certain degree of error in curve deconvolution technique.

(2) On the lower-energy side of both the KLL and 2s signals, there exists a weak signal because of the surface plasma. This needs to be corrected to the main signals. The correction term is smaller for 2s than for KLL.

Thermite mixture surface analysis

The overall XPS spectrum of thermite powders aged at 180°C is shown in Fig. 1b. Comparing Fig. 1a to 1b, it is obvious that in thermite powders, Cu $2p_{1/2}$, Cu $2p_{3/2}$, and Cu $L_3M_{4,5}M_{4,5}$ of Cu_2O were detected. Unfortunately Cu 3s and Cu 3p happen to be at the same position as Al 2s and Al 2p, respectively.

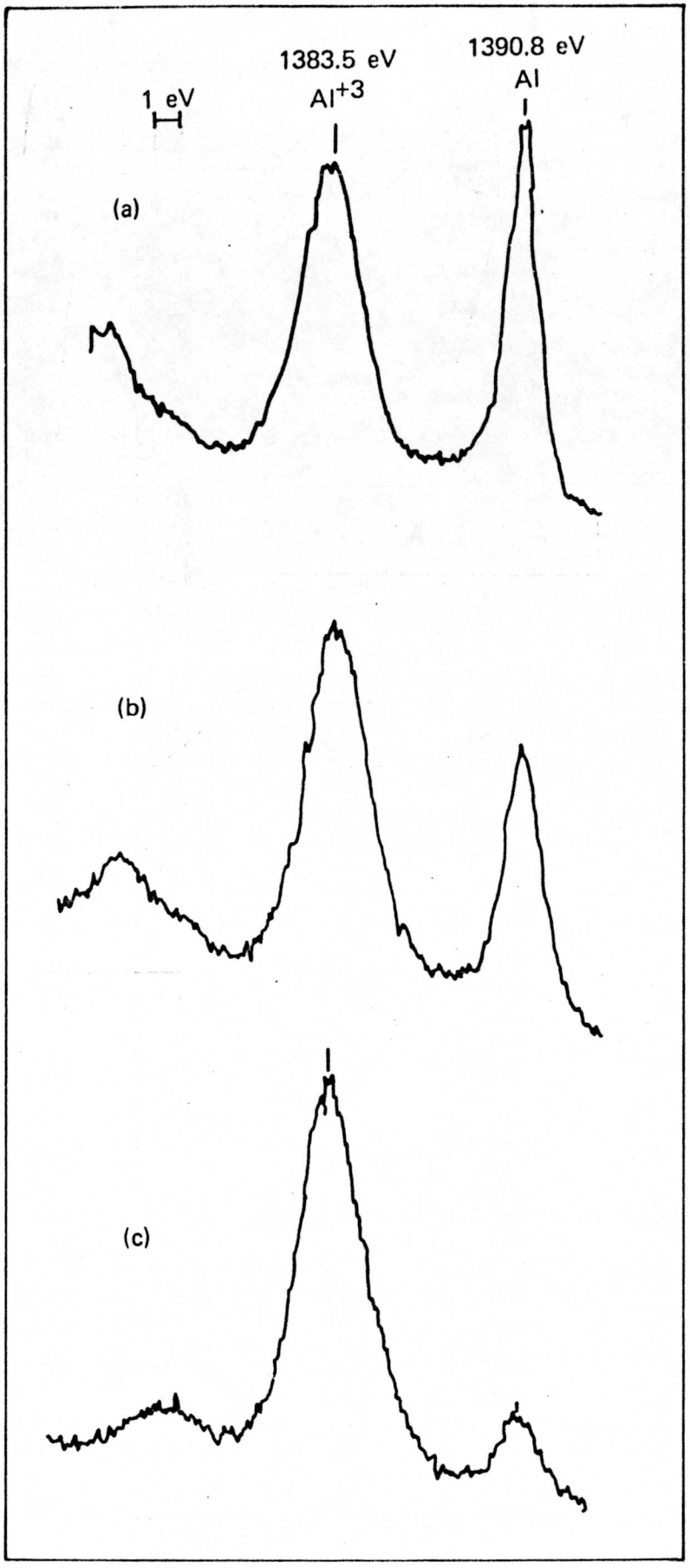

Fig. 4. Al-KLL spectra of: (a) aluminum flakes stored at room temperature, (b) aluminum flakes after mixing with Cu_2O to form thermites at room temperature, (c) thermite powders aged at 180°C for 91 days in dry air.

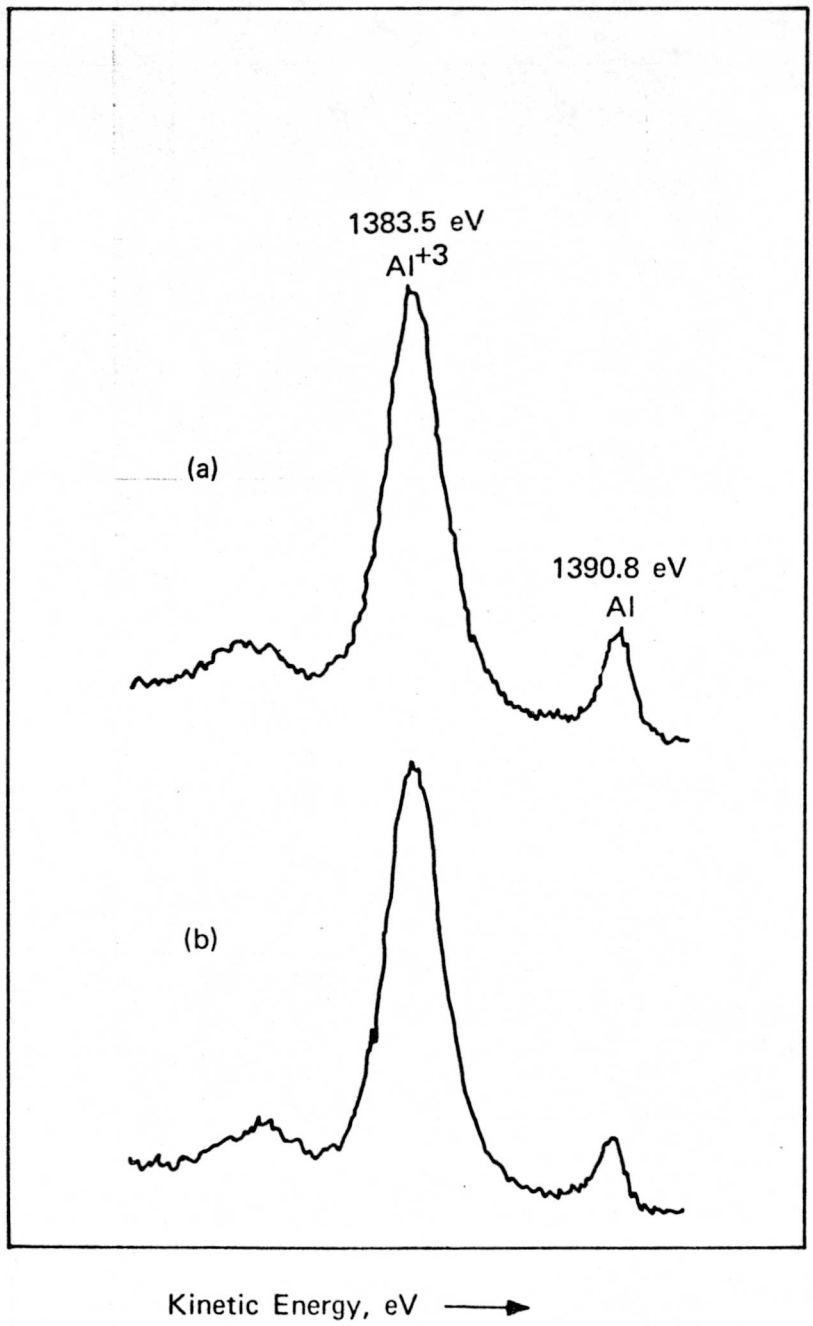

Fig. 5. Al-KLL Auger spectra of: (a) Al/Cu_2O thermite pellet after pressing at 425°C, (b) pellet aged at 180°C for 27 days in dry air.

The carbon 1s signal from thermite powder is approximately one-fourth of the carbon 1s signal from aluminum flakes. Also, it is skewed when compared to that signal from aluminum flakes. After the sample (either in dry air or argon) was heated to 180°C, the signal was reduced almost to background. This suggested that a small degree of oxidation occurred during the mixing and the heating, thereby removing stearic acid.

Fig. 4 shows Al-KLL Auger of (a) aluminum flakes before mixing with Cu_2O, (b) aluminum flakes after mixing with Cu_2O at room temperature to form thermite powders, and (c) thermite powders aged at 180°C in dry air for 91 days. Just from this figure, it is obvious that oxide film thickness increases after mixing and further increases during aging.

Results derived from the Al-KLL Auger for thermite powders are tabulated in Table 2. The oxide film of the powders at room temperature was found to be about

TABLE 2

Aluminum-KLL Auger results for aluminum/cuprous oxide thermite aged at various conditions

Sample	d_o (Å)
Powder in air at room temperature	10.8
Powder in air 40 days at 180°C	21.4
Powder in air 91 days at 180°C	24.8
Powder in air 136 days at 180°C	23.8
Powder in argon 136 days at 180°C	22.1
Air, room temperature, pellet	22.3
Air 27 days at 60°C, pellet surface	25.4
Air, 27 days at 60°C, fractured pellet	23.7
Air, 27 days at 180°C, pellet surface	25.7
Argon, 131 days at 180°C, pellet surface	28.1
Argon, 131 days at 180°C, fractured pellet	23.4

11 Å, which means that just mixing aluminum powder and Cu_2O at room temperature creates an oxidation reaction that increases the oxide layer by 2 Å. The oxide layer increases to about 21 Å for the first 40 days at 180°C in air and levels off after 3 mo at 24-25 Å. In argon at 180°C for 136 days, the oxide layer was found to be about 22 Å.

Fig. 5 shows the Al-KLL Auger of a thermite pellet (a) after pressing, and (b) after aging at 180°C for 27 days in dry air. Comparing (a) to (b) indicates that aging of the pellet shows an insignificant change in the oxide layer thickness; but comparing Fig. 5a to Fig. 4b proves that pressing of the pellet indeed induces some oxidation and increases the oxide layer considerably.

In order to press thermite pellets, it was necessary to bring the temperature up to 425°C. This increased the oxide film from about 11 to about 22 Å. Further aging of the pellets caused little increase in oxide layer thickness - no more than 6 Å in 131 days at 180°C. As expected, the oxide layer in the bulk part of the pellet was found to be thinner than that on the surface. The results are shown in Table 2.

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