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SCANNING AUGER MICROSCOPY OF CONSOLIDATED Al/Cu_2O THERMITE PELLETS

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ABSTRACT

The outer and the fractured surfaces of hot-pressed Al/Cu_2O pellets were investigated by scanning Auger microscopy (SAM). The surface images and elemental pictures of aluminum and copper are illustrated. Auger spectra of the outer surface show the existence of carbon, chlorine, oxygen, and sodium as contaminants. Auger mapping of the grains gives a clear picture of the Cu_2O particles and the general continuum of the aluminum. These pictures compare well with scanning electron micrographs taken previously of similar Al/Cu_2O pellets. In-depth elemental profiling by sputter-etching illustrates that carbon, sodium, and chlorine are surface contaminants. The analysis of the fractured surface verified the presence of an interfacial region between the aluminum and the Cu_2O of at least 100 Å that was caused by the pelletization process at elevated temperatures.

INTRODUCTION

At a previous meeting in this series (ref. 1), we reported aluminum oxide (Al_2O_3) surface film growth on aluminum particles used in Al/Cu_2O thermites during blending, hot-pressing, storage and accelerated aging studies. The results indicated that surface oxide films on aluminum as measured by x-ray-induced Al K-LL Auger signals of Al^{+3} and Al^{0} doubled in thickness after the thermite powders were hot-pressed at 425°C for 15 min under nitrogen. However, this layer of surface oxide was found to protect the aluminum fuel of the thermite pellets, and further aging of the pellets at 180°C for over 4 months did not change the oxide film thickness (refs. 1,2).

In pyrotechnic reactions, such as in the Al/Cu_2O thermite system, surface chemistry of fuels and oxidizers were proved to play an important role in reaction mechanism and ignition kinetics (ref. 3). In the case of titanium, the presence of a native surface oxide film and its dissolution prior to ignition has been shown

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to play an important role in the pyrotechnic reaction mechanism (refs. 3,4). X-ray photoelectron spectroscopy (XPS) Ti 2p results and high resolution Auger electron spectroscopy (AES) Ti LMM scans showed that a titanium oxide (TiO_2) film is present on the titanium surface. A layer of titanium suboxide (TiO_x, $0<x<2$) was also observed between the Ti metal and the TiO_2 film. During heating processes, oxygen was found to diffuse into the metal and the diffusion rate was observed to increase sharply at about 350°C. A metallic surface was observed just prior to the ignition temperature. Surface conversion from TiO_2 to Ti through TiO_x has been observed. A similar mechanism has also been observed in TiH_x ($x = 1.15, 1.62$) pyrofuels (ref. 5). However, the temperature at which the rate of oxygen was found to increase sharply was about 500°C for the TiH_x samples. The higher temperature for oxygen dissolution on TiH_x is believed to be due to the outward diffusion of hydrogen inhibiting the inward diffusion of oxygen at temperatures below 500°C.

In light of the fact that aluminum surface oxide in the Al/Cu_2O system remains intact through heating cycles to 1000°C, it is unlikely that the ignition mechanism in Al/Cu_2O is oxygen dissociation of surface oxide to provide a metallic surface for reaction; thus, oxide film increase in pelletizing is likely to involve a different mechanism. Differential scanning calorimetry (DSC) of aluminum powder in copper pans indicated formation of an alloy of Al/Cu during heating and an endothermic phase change of this alloy at 540°C (ref. 3). DSC of thermites shows this endotherm and a strong ignition exotherm at 545°C, while in thermite powder two exotherms were observed at ~600°C and ~850°C. Consequently, we can conclude that the presence of the endotherm in the DSC curve for consolidated thermite indicates that the Al/Cu alloy was formed during the consolidation process. Ignition of the thermite powder seems to depend on heat generated by aluminum diffusing to the surface of particles for reaction. However, if the thermite has been consolidated, the high pressures in a nitrogen blanket exclude air, while the elevated temperatures generate free aluminum at the particle surface. This aluminum can then alloy with copper from the Cu_2O. Ignition can occur due to heat generated by the oxidation of the alloy rather than of the aluminum. The phase change at 540°C apparently favors the alloy oxidation reaction, which can generate the heat to achieve ignition of the thermite reaction thought to occur at higher temperatures (perhaps the second exotherm in the DTA of the powder).

In this paper, we report the study of the interfacial region of aluminum and Cu_2O by scanning Auger microsocopy.

EXPERIMENTAL PROCEDURES

Sample preparation

Theoretically stoichiometric thermite mixtures of 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 one hour. Aluminum flakes were used as received and Cu_2O powders were sieved through a 400-mesh screen to remove oversized particles. For outer surface analysis, thermite pellets 6 mm in diam and 2 mm thick were hot pressed with preheated graphite dies at 425°C and 12,000 psi for 15 min under dry nitrogen (ref. 6). The density of the pellets is about 90% of theoretical density. For the fractured surface study, the samples were prepared by first hot pressing Cu_2O and then pressing Al flakes into Cu_2O pellets. The interface regions were investigated after the Al and Cu_2O portions separated.

Scanning Auger microprobe

The SAM spectrometer used in this study is a Physical Electronics Phi Model 590. A heated lanthanum hexaboride (LaB_6) filament is used for the source of monoenergetic electrons. The scanning electron gun has three lenses which allow for sufficient focusing power to observe features as small as 0.2 μm. The electron gun operates at beam voltages up to 10 kV. For this report, data were taken with an electron gun operating at 8 kV electron beam energy and 2 nA electron beam current. Typical electron beam current densities were $<1\ \text{A}/\text{cm}^2$. Two Auger detection modes were used in this study: the standard dN(E)/dE mode generated through a lock-in amplifier and the digital N(E) mode. The Al/Cu_2O thermite specimens were sputter-etched with a differentially pumped ion gun.

RESULTS AND DISCUSSION

Pellet outer surface

Figure 1 shows a scanning electron image of the outer surface of the Al/Cu_2O pellet (Mound Sample #1366) amplified 1000 times; note that the grains of aluminum and Cu_2O can be clearly observed. A wide beam Auger electron spectrum of this surface is shown in Fig. 2. The data in Fig. 2 clearly show the presence of the surface contaminants: chlorine, carbon, and sodium. From the observed pattern of the aluminum K-LL Auger spectrum, one can conclude that the surface aluminum is an oxide of aluminum (ref. 7). Also, the aluminum/copper signal ratio is larger than expected from the stoichiometric mixture. This measured ratio is in agreement with previous results from XPS (refs. 1,2).

Figs. 3-5 show the Auger outer surface maps of carbon, aluminum, and copper. The lighter areas signify an enriched area of the specific element. Fig. 4 indicates that the surface of the pellet consists mainly of aluminum; this is due to the low surface tension of aluminum at 425°C as compared to Cu_2O or copper

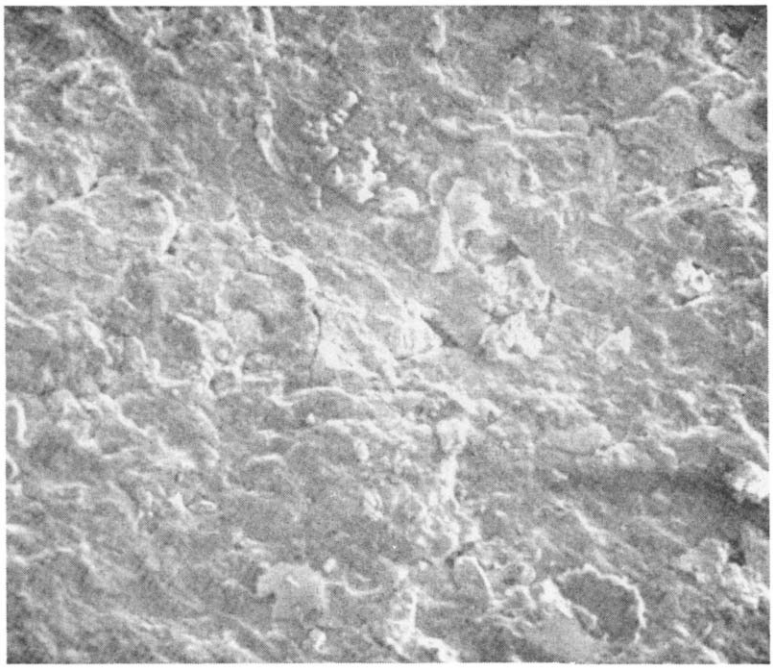

Fig. 1. Scanning electron image of Mound Al/Cu_2O pellet #1366 (1000X).

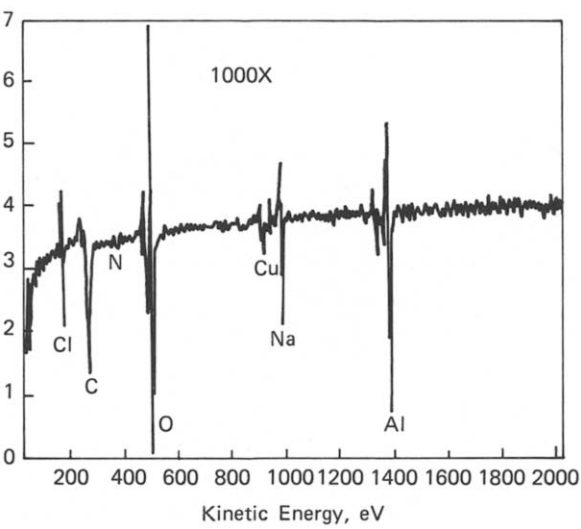

Fig. 2. A wide beam Auger electron spectrum of the surface of an Al/Cu_2O pellet (Mound Sample No. 1366).

Fig. 3. Carbon Auger map of outer surface of pellet #1366 (1000X).

Fig. 4. Aluminum Auger map of outer surface of pellet #1366 (1000X).

metal. The surface tension is the measure of the work (or energy) required to create a fresh surface. A total component distribution of the surface can be easily constructed from the combination of the three spectra of Figs. 3-5.

These Auger elemental images are further verified by Auger electron spectra taken in each of the enriched regions. Fig. 6 is a computer-enhanced aluminum map from the region of Fig. 4; Fig. 4 was taken at 1000X and Fig. 6 at 3000X. Auger electron spectra of points 1 and 2 in Fig. 6 indicate that these points are indeed rich in Cu_2O and Al (mostly Al_2O_3), respectively, as shown in Figs. 7 and 8.

A three-dimensional analysis can be accomplished by the surface sputtering technique. Point 3 in Fig. 6 is an aluminum-rich area as can be seen from the figure. The Auger electron in-depth elemental profile, shown in Fig. 9, illustrates that this point is about 80-85 at. % aluminum and about 6-10 at. % copper. After sputtering has been applied at a rate of 50 Å/min, however, there is a decrease in aluminum and an increase in copper. These data hint that under the enriched aluminum surface layer, there exists a stoichiometric cuprous oxide particle and that the thickness of the surface-enriched layer of aluminum is >1000 Å.

Fractured surface

A scanning electron micrograph of a fractured surface of another pellet (Mound Sample #1365) is shown in Fig. 10, and computer-enhanced copper and aluminum mappings are illustrated in Figs. 11 and 12, respectively. Auger electron spectra show the presence of Cu_2O particles at both Point 1 and Point 2. Analysis of Point 2 following removal of 100 Å (Fig. 13) shows little difference from the analysis before sputtering.

At Point 3, a mixed region of aluminum and copper oxides was detected (Fig. 14). This mixed region of aluminum and copper oxides resulted from the hot-pressing process. Auger analyses following continuous sputtering of the surface (after 25 Å, after 75 Å, and after 100 Å removal) show the coexistence of aluminum and copper oxides, with a continuously increasing copper signal. The AES spectrum after 100 Å removal is reproduced in Fig. 15. This analysis suggests that there is a layer of the mixed or reacted aluminum and Cu_2O surrounding a large grain of Cu_2O.

CONCLUSION

We have verified in this study that 1) the enriched-aluminum surface layer of a pressed pellet is >1000 Å thick, and 2) an interfacial region is formed between the aluminum metal and the cuprous oxide during the hot-pressing operation. The interfacial region measured at least 100 Å in thickness.

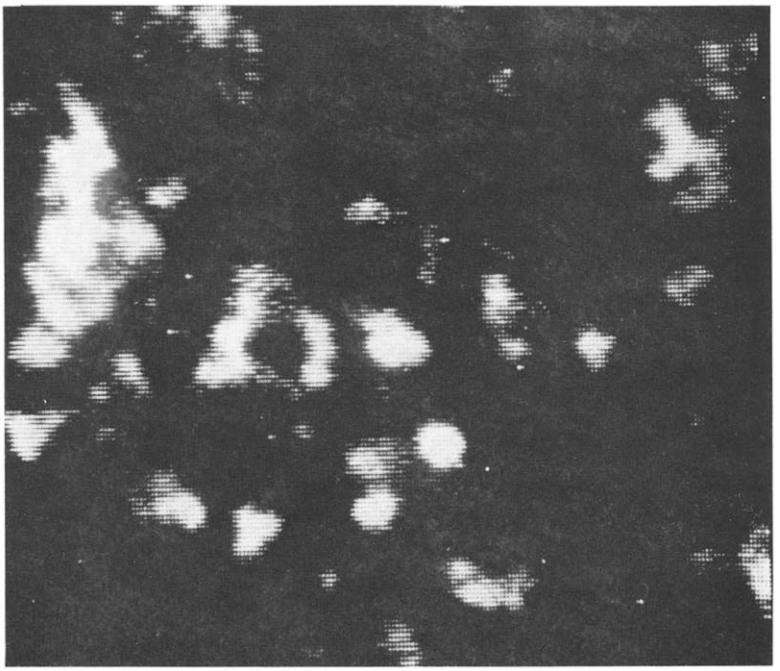

Fig. 5. Copper Auger map of outer surface of pellet #1366 (1000X).

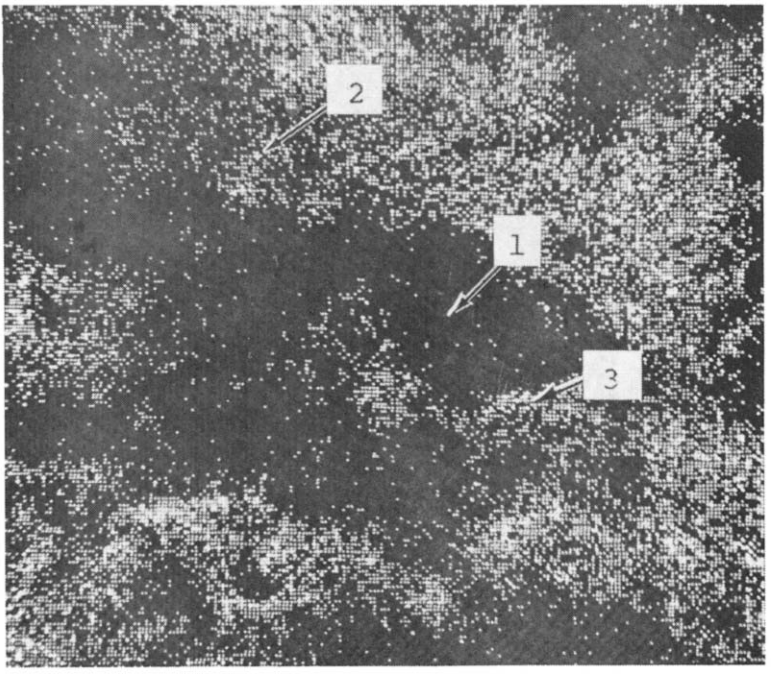

Fig. 6. Computer enhanced aluminum Auger map (3000X) of a region in Figure 4.

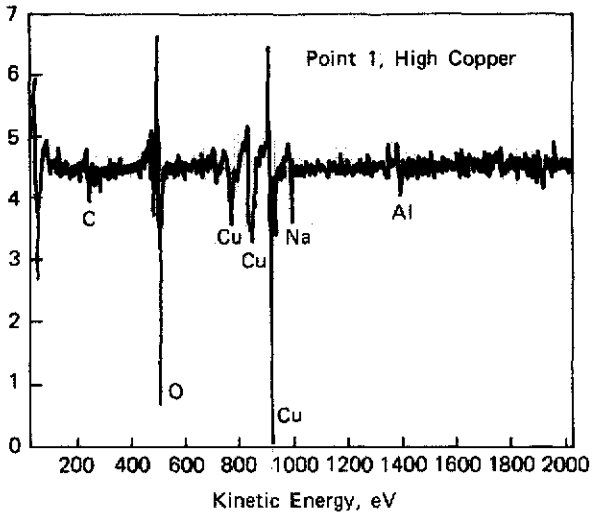

Fig. 7. Auger electron spectrum of Point 1 in Figure 6 shows it is rich in Cu_2O.

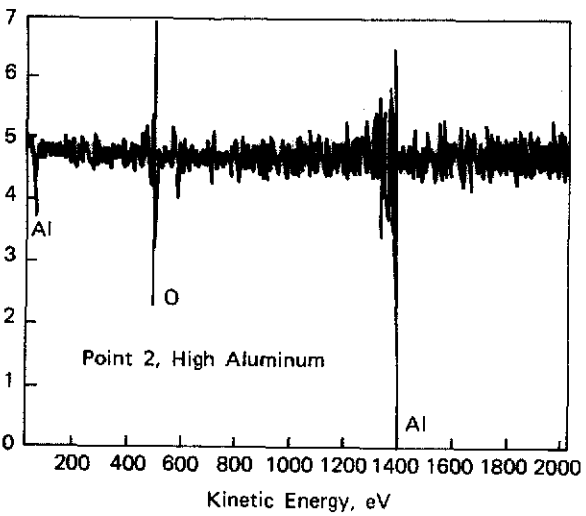

Fig. 8. Auger electron spectrum of Point 2 in Figure 6 shows it is rich in Al_2O_3 with some Al metal.

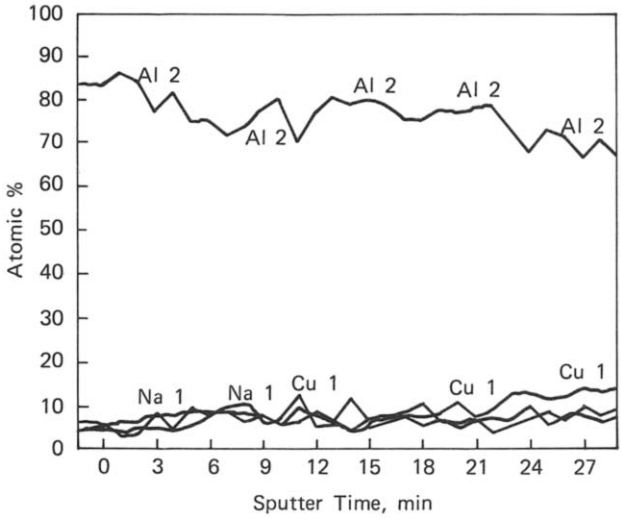

Fig. 9. Auger electron spectroscopic profile of Point 3 in Figure 6 (50 Å/min).

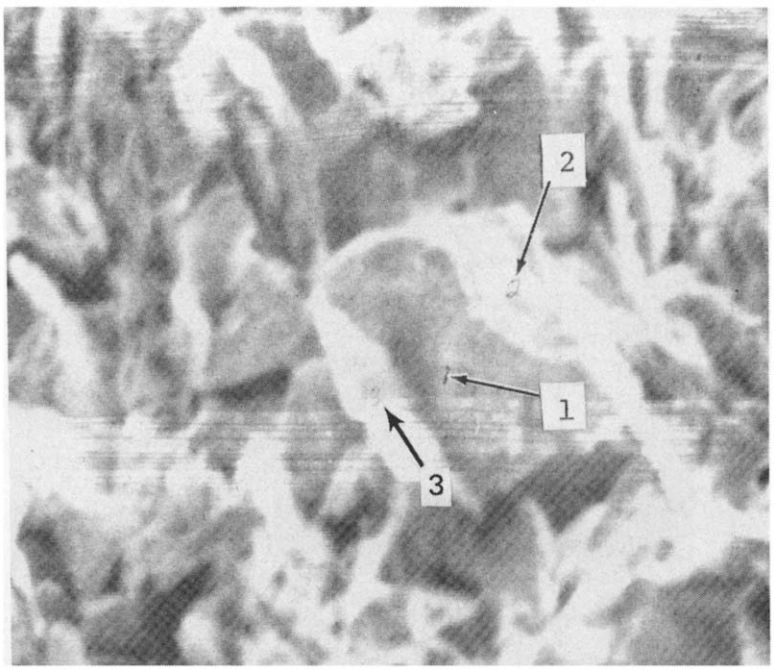

Fig. 10. Scanning electron micrograph of fractured surface of Mound Al/Cu_2O pellet #1365 (3000X).

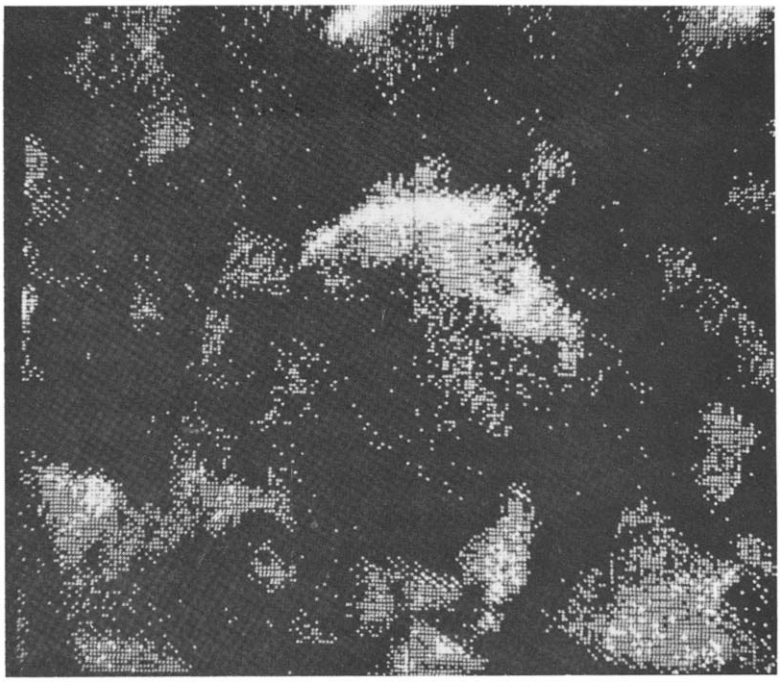

Fig. 11. Computer enhanced copper Auger map of the fractured surface.

Fig. 12. Computer enhanced aluminum Auger map of the fractured surface.

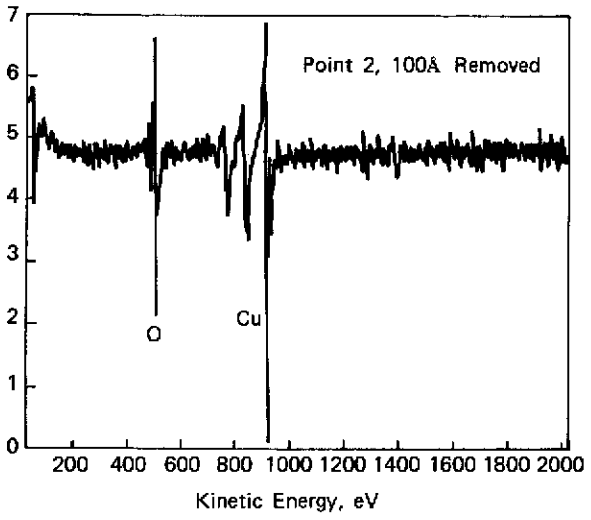

Fig. 13. Auger elctron spectrum of Point 2 in Figure 10 after removal of 100 Å of the surface.

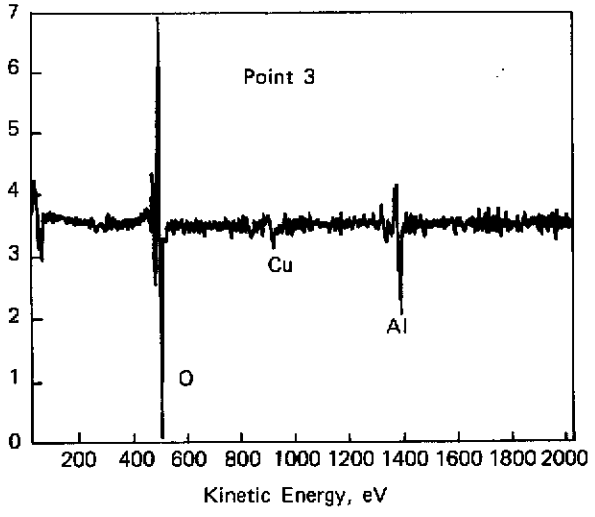

Fig. 14. Auger electron spectrum of Point 3 in Figure 10 shows it rich in Al_2O_3.

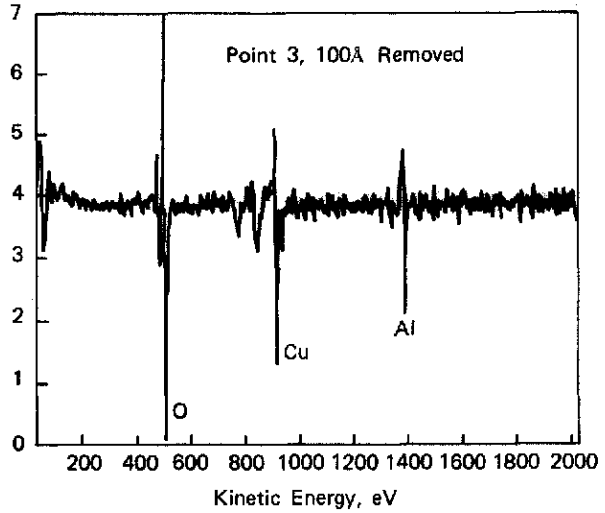

Fig. 15. Auger electron spectrum of Point 3 in Figure 10 after removal of 100 Å of the surface.

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REFERENCES

1 P. S. Wang, L. D. Haws, W. E. Moddeman, and A. Rengan, "Al/Cu_2O Thermite Compatibility Studies by X-ray Photoelectron and X-ray Induced Auger Spectroscopy," in Proc. Joint Symp. on Compatibility of Plastics/Materials with Explosives and Processing Explosives, Blacksburg, Virginia, October 14-16, 1980, MLM-2765(OP).

2 W. E. Moddeman, A. Rengan, P. S. Wang, and L. D. Haws, "Surface Studies of an Aluminum/Cuprous Oxide Thermite Mixture by X-ray Photoelectron and Auger Spectroscopies," in Proc. 10th Symp. on Explosives and Pyrotechnics, San Francisco, February 14-16, 1979, MLM-2627(OP).

3 W. E. Moddeman, L. W. Collins, P. S. Wang, and T. N. Wittberg, "Role of Surface Chemistry in the Ignition of Pyrotechnic Materials," in Proc. 7th Int. Pyrotechnics Conference, Vail, Colorado, July 14-18, 1980, MLM-2708(OP).

4 T. N. Wittberg, W. E. Moddeman, L. W. Collins, and P. S. Wang, "The Dissolution of Native Oxide Films on Titanium for Pyrotechnic Applications," in Proc. 8th Int. Vacuum Congress, Cannes, France, September 22-26, 1980, MLM-2754(OP).

5 T. N. Wittberg and P. S. Wang, "The Dissolution of Surface Oxide Layers on Titanium and Titanium Subhydride Between 25° and 700°C," in Proc. 11th Symp. on Explosives and Pyrotechnics, Philadelphia, Pennsylvania, September 15-17, 1981, MLM-2856(OP).

6 L. D. Haws, M. D. Kelly, J. H. Mohler, and A. Latkin, "Consolidated Al/Cu_2O Thermites," in Proc. 6th Int. Pyrotechnic Seminar, Estes Park, Colorado, July 17-21, 1978, MLM-2531(OP).

7 L. E. Davis et al, Handbook of Auger Electron Spectroscopy, 2nd edn., Physical Electronics Industries, Inc., Eden Prairie, Minnesota, 1978.