Secondary Electron Emission from Copper-Beryllium (4%) Surface by Bombardment of Various Positive Ions

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According to the development of the mass spectrometric investigations, the necessities for the measurements of the minute ion intensity are rapidly increasing. The secondary electron multiplier has now widely been used as an excellent ion detector for the measurements of ionization potentials and the microanalysis of many isotopes. Many reports on the secondary electron emission from the metal surfaces by the bombardment of high energy ions were already published. But unfortunately, some results of them disagree with each other(1,2), and these discrepancies might be caused by the different surface conditions of the ion targets for the secondary electron emission.

Recently, Hagstrum(3-6) has reported the many important results of the Auger ejection process of secondary electrons from the atomically clean surfaces of transition metals by the bombardment of the noble gas ions, and he suggested that the existence of the adsorbed layer causes the remarkable influence on the mechanism of the secondary electron ejection. But the target surfaces are not always atomically clean under the ordinary operating conditions, and the influence of the adsorbed layer seems considerably complicated since the semiconductor surfaces are usually used for obtaining the large electron yield.

The characteristics necessary for the secondary electron multiplier are the large electron yield per impinged ion or electron and the excellent stability for the electron yield under the usual operating conditions. The electron yield mainly depends upon the following factors:

(1) the mass, energy, electronic charge and configuration of the incident particle;

(2) the chemical and physical properties of the metal surface; and

(3) the angle with which the incident particle strikes the metal surface.

The present investigation was undertaken in order to find the optimum condition of the preparation of the sensitive and stable surface of the copper-beryllium target suitable for the secondary electron multiplier. This paper reports the main results of the following studies:

(1) the dependency of the electron yield of the non-activated and activated target surfaces upon the kinetic energy of various noble gas and hydrocarbon ions;

(2) the determination of the surface structures of the ion targets by means of electron diffraction analysis; and

(3) the influence of the temperature of treatment upon the electron yield and the stability of the target surfaces.

Experimental

Mass Analyser and Ion Targets. — The present experiments were performed by a mass spectrometer self-constructed in our laboratory. This mass spectrometer is a single focusing 90° sector type and the radius of curvature of the ion path is 135 mm., and the ion source of the usual electron bombardment type was installed in this instrument. In the present experiments two kinds of simple detectors were used. The constructions of the target assembly of them are schematically shown in Figs. 1a and 1b.

In Fig. 1a, T_1 indicates the ion target, C_1 the collecting plate of secondary electrons, S_1 the enclosing cage of the detector, and E_1 the collector slit. The other detector shown in Fig. 1b was constructed in order to measure the electron yield of the copper-beryllium surface by the bombardment of secondary electrons. But in the present experiments this detector shown in Fig. 1b was also used for the measurements of the electron yield by the bombardment of various positive ions. In Fig. 1b, T_2 indicates the ion traget, D and C_2 the collecting plates of sencondary electrons, S_2 the enclosing cage of the detector, E_2 the collector slit.

The geometries of the ion tragets (T_1 and T_2) and the collecting plate of secondary electrons (D) are similar to those of the electron multiplier of the Nier type(7). The width of the collector slit was fixed to 2 mm., while the width of the exit slit of

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1) M. G. Inghram, "Mass Spectroscopy in Physical Research", NBS Circular No. 522, 257 (1953).

2) M. G. Inghram, "A Handbook on Mass Spectroscopy", National Academy Sciences (1954), p. 41.

3) H. D. Hagstrum, *Phys. Rev.* **89**, 244 (1953).

4) H. D. Hagstrum, ibid., **91**, 543 (1953).

5) H. D. Hagstrum, ibid., **96**, 325, 336 (1954).

6) H. D. Hagstrum, ibid.. **104**, 317, 672, 1516 (1956).

7) K. S. Quisenberry, T. T. Scolman and A. O. Nier, ibid., **102**, 1071 (1956), W. H. Johnson, Jr. and A. O. Nier, ibid., **105**, 1014 (1957).

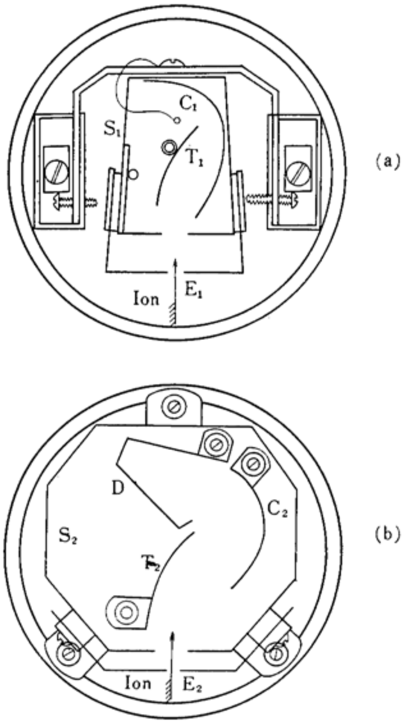

Fig. 1. Schematic diagrams of the ion collectors of the mass spectrometer. T_1(a) and T_2(b) are the ion targets, C_1 (a) and D(b) are the electron collectors, C_2(b) is Cu-Be dynode, S_1(a) and S_2(b) are the enclosing cages, and E_1(a) and E_2(b) are the collector slits.

the ion source is 0.2 mm. The ion targets were formed from the copper-beryllium plates* of 0.16 mm. in thickness, and the collecting plates of secondary electrons, the enclosing cages and the collector slits were all shaped from the molybdenum plates of 0.15 mm. in thickness.

For the measurements of the ion currents the collector slit (E_1 or E_2) and the ion target (T_1 or T_2) were kept to the earth potential and the electron suppressor voltage of -20 V. was supplied to all collecting plates (C_1 and S_1 in Fig. 1a ; D, C_2 and S_2 in Fig. 1b). On the other hand, for the measurements of the secondary electron currents the collecting plates of secondary electrons were all kept to the earth potential and the potential of -270 V. was supplied to the ion target. It has been experimentally confirmed that these two types of detectors show the same value in the electron yield under the same experimental conditions.

A UX-54 tube was used as the primary tube of the d. c. amplifier, and the output currents were recorded by two galvanometers that have different sensitivities. The end vacuum under the ordinary experimental conditions was somewhat better than 1×10^{-6} mm Hg.

Treatment of Ion Targets. — The non-activated targets were treated in the following manner. After being tempered, the alloy plates were mechanically polished with the fine emery papers of No. 0000 to 0005. After that the ion targets were formed and then electropolished in the polishing solution** for about one minute.

The treatment of activation of the ion targets was carried out in a quartz tube (25 mm. in outer diameter and 300 mm. in length) which was connected by the water-cooled taper joint to the vacuum system, the reservoir of purified oxygen and a McLeod gauge. The quartz tube was heated in an electric furnace and the temperature was measured by a copper-constantan thermocouple enclosed in this quartz tube. The electropolished targets were put into the quartz tube and evacuated to lower than 5×10^{-6} mmHg at about 800°C for three hours. After the evacuation the temperature was lowered to each required temperature (i. e. 350, 420, or 480°C), and then the known quantity of oxygen was introduced into the quartz tube. The initial pressure of oxygen for each treatment was about 2×10^{-2} mmHg, and the pressure decrease in each time was measured by a McLeod gauge.

The results are shown in Fig. 2. As seen in Fig. 2, the present results indicate that the initial rate of the pressure decrease is independent of the temperature of treatment. After the treatment of 20 min. the quartz tube was evacuated and gradually cooled to the room temperature, and then the targets were taken out and mounted in the ion collector of the mass spectrometer.

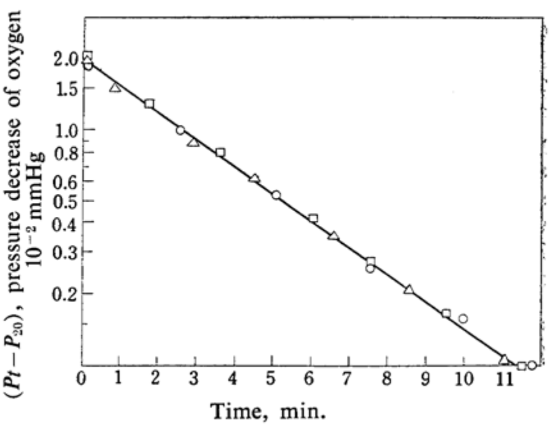

Fig. 2. Rate of the pressure decrease of the oxygen, by the treatment of the Cu-Be at the various temperatures: □; 350°C, △; 420°C and ○; 480°C.

Determination of Surface Structure. — The surface structure of the non-activated and activated ion targets was analysed by means of a commercial Hitachi E. D. C. type electron diffraction apparatus.

Gaseous Materials. — Oxygen was prepared by the thermal decomposition of potassium permanganate, and purified by passing through the trap

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* The copper-beryllium plates of 0.16 mm. in thickness were prepared from a copper-beryllium(4%) alloy rod of the Beryllico Co., U. S. A.

** The electropolishing solution was prepared by mixing four volumes of phosphoric acid, four volumes of glycerin and three volumes of water.

cooled by liquid nitrogen. Spectroscopically pure argon and neon of the Teikoku Oxygen Co. were used without any further purification. The mass spectrometric analyses of these gaseous samples revealed that the total impurities were less than 0.005 per cent in volume. The research grade ethylene and ethane of the Philips Petroleum Co. were used in the present experiments, and the purity was also checked by means of the mass spectrometer.

Results

Surface Structure of Copper-Beryllium Targets. — The surface structures of the copper-beryllium targets examined by the electron diffraction apparatus are summarized in Tables I and II. The main results of the analysed interplanar distances for the three kinds of ion targets — i. e. (a) tempered at about 800°C and mechanically polished, (b) tempered, mechanically polished, and then electropolished, and (c) tempered, mechanically polished, electropolished, and then bombarded by various positive ions for five hours — are listed in Table I together with that of Cu, Cu_2O and CuO by X-ray diffraction analysis[8] for the sake of comparison. As seen in Table I, the oxide films of copper (mainly Cu_2O) are partially left on the mechanically polished surface (a). The electropolished surface (b) shows that the mechanically polished surface was re-oxidized by electropolishing, while the surface bombarded by various positive ions (c) indicates that the electropolished surface was partially reduced during the prolonged bombardments of various positive ions.

TABLE I. INTERPLANAR SPACINGS (Å) OF Cu-Be SURFACES MEASURED BY ELECTRON DIFFRACTION

(1) NOT TREATED SURFACES

(a) Mechanical polished surface, (b) electropolished surface, (c) after ion irradiation of the electropolished surface, and included the X-ray data of Cu, Cu_2O and CuO.

(a)	(b)	(c)	Cu	Cu_2O	CuO
2.998	2.501	2.992	2.08	3.00	2.51
2.443	2.166	2.623	1.81	2.45	2.21
2.207	1.758	2.395	1.277	2.12	1.70
2.010	1.522	2.180	1.228	1.51	1.57
1.816	1.273	1.766	1.089	1.283	1.50
1.540	1.131	1.649	1.043	1.065	1.408
1.356	0.956	1.577	0.905	0.971	1.370
1.235	0.874	1.176		0.869	1.254
1.155				0.819	1.159
1.070					1.086
1.030					1.007
0.864					0.855

TABLE II. INTERPLANAR SPACINGS (Å) OF Cu-Be SURFACES MEASURED BY ELECTRON DIFFRACTION

(2) TREATED SURFACES BY OXYGEN

Included the X-ray data of BeO and CuO.

Treated temperature			BeO	CuO
480°C	420°C	350°C		
2.477	2.470	2.476	2.34	2.51
2.283	2.317	2.290	2.19	2.31
2.218	2.161	2.172	2.06	1.85
2.096	1.993	2.031	1.59	1.70
2.001	1.565	1.497	1.350	1.57
1.808	1.523	1.313	1.239	1.50
1.566	1.315	1.272	1.170	1.408
1.429	1.200	1.217	1.150	1.37
1.312	1.124	1.174	1.130	1.298
1.275	1.060	1.123	1.032	1.254
1.171	0.919	1.057	0.915	1.159
1.163	0.888	1.036	0.884	1.086
1.123	0.855	0.969	0·870	1.007
1.074	0.796	0.863	0.822	0.978
1.053	0.753	0.796	0.780	0.885
1.038		0.741	0.758	
0.975				
0.874				
0.849				
0.789				
0.758				

The interplanar distances analysed for the activated surfaces treated at various temperatures are summarized in Table II together with the X-ray diffraction data[8] of BeO and CuO. As seen in Table II, the difference in the surface structure between each temperature of the treatment is not clear, but the diffraction patterns peculiar to BeO are clearly observed for all specimens. This fact may be interpreted to mean that beryllium ions (or atoms) in the alloy rapidly migrate through the lattice and arrive at the surface at these temperatures of the treatment, and that since they easily react with oxygen and are fixed as beryllium oxide the concentration of this compound in the neighborhood of the alloy surface will be considerably increased by the treatments of activation.

Dependency of Electron Yield upon Ion Kinetic Energy.—In Figs. 3 and 4, the electron yield for the non-activated and activated (treated at 420°C) target surfaces is plotted as a function of the kinetic energy of singly- and doubly-charged argon ions and the five different ions from ethylene, respectively. The variation of the electron yield with the kinetic energy of the parent and fragment ions from ethane for the activated target surface treated at 420°C is shown in Fig. 5. Fig. 6. shows

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[8] K. Kubo, "The Method of Chemical Analysis by Meanes of X-ray Diffraction", Shukyosha Co., Tokyo (1947), pp. 118, 152, 156.

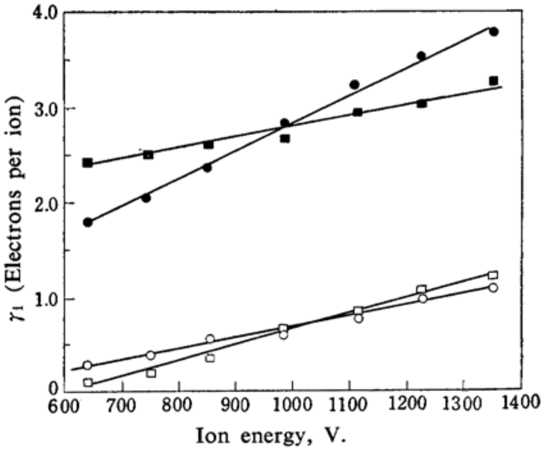

Fig. 3. Plot of experimental data giving electron yield γ_i, as a function of ion kinetic energy for A^+(● activated, and ○ non-activated) and A^{2+}(■ activated and □ non-activated) on 420°C activated and non-activated Cu-Be targets.

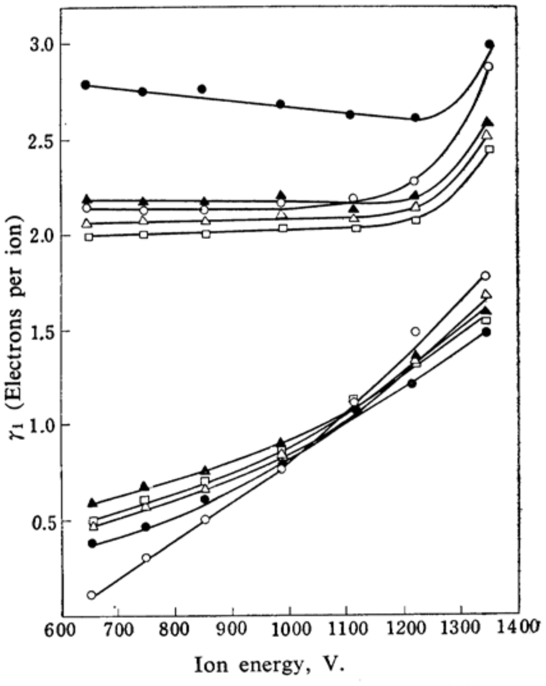

Fig. 4. Plot of experimental data giving electron yield γ_i, as a function of ion kinetic energy for parent and fragment ethylene ions; upper five curves are data on the 420°C activated Cu-Be target and lower are data on the non-activated Cu-Be target. ○; $C_2H_4^+$, △; $C_2H_3^+$, □; $C_2H_2^+$, ▲; C_2H^+, and ●; C_2^+.

the influence of the temperature of the treatment (480, 420 and 350°C) on the variation of the electron yield with the kinetic energy of singly- and doubly-charged neon ions.

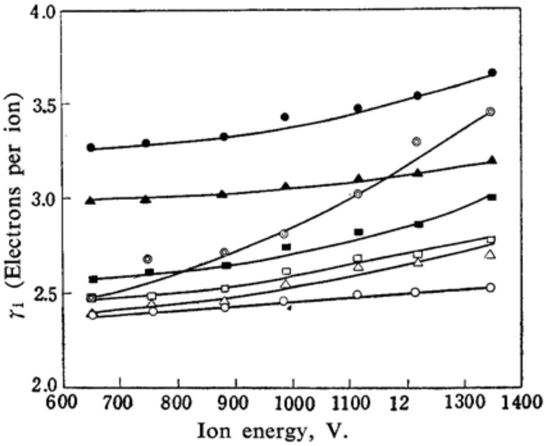

Fig. 5. Plot of experimental data giving electron yield γ_i, as a function of ion kinetic energy for parent and fragment ethane ions: ◎; $C_2H_6^+$, ■; $C_2H_5^+$, ○; $C_2H_4^+$, △; $C_2H_3^+$, □; $C_2H_2^+$, ▲; C_2H^+, and ●; C_2^+, on activated target treated at 420°C.

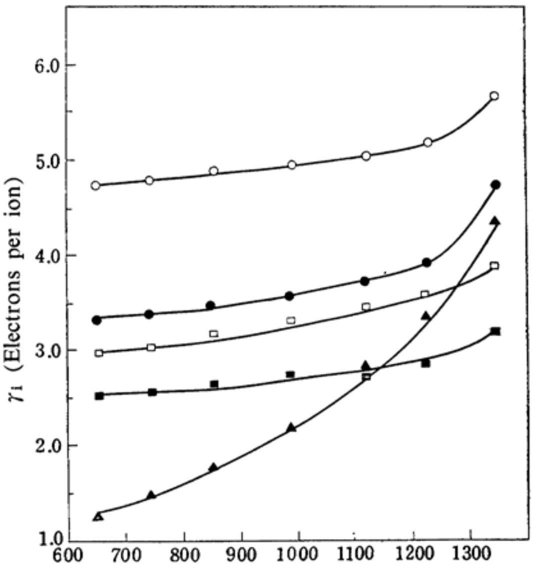

Fig. 6. Plot of experimental data giving electron yield γ_i, as a function of ion kinetic energy for singly- and doubly-neon ions on activated target treated at various temperatures.
○; Ne^{2+}, 420°C, ●; Ne^+, 420°C, □; Ne^{2+}, 350°C, ■; Ne^+, 350°C, ▲; Ne^+, 480°C.

Stability of Electron Yield by Ion Impacts.—Under the present experimental conditions, the electron yield for the non-activated surface gradually decreased and reached about 80 per cent of its initial value by the prolonged

TABLE III. THE SECONDARY ELECTRON YIELDS (γ_i) AND THE IONIZATION POTENTIALS (I. P.) AND THE APPEARANCE POTENTIALS (A. P.)

The values of γ_i are shown for 980 volts ion energy and for the target surface activated at 420°C.

	Ethane			Ethylene	
Ion	I. P.[9] eV.	γ_i electrons/ion	A. P.[9] eV.	γ_i electrons/ion	A. P.[9] eV.
$C_2H_6^+$	11.6	2.75	11.6	—	—
$C_2H_5^+$	8.7	2.90	12.9	—	—
$C_2H_4^+$	10.8	2.50	12.1	2.20	10.8
$C_2H_3^+$	9.9	2.55	15.2	2.09	14.1
$C_2H_2^+$	11.2	2.50	15.0	2.04	13.4
C_2H^+	11.3	3.05	27.0	2.20	19.2
C_2^+	—	3.05	31.5	2.70	26.4

bombardments of the various positive ions mentioned above for five hours. On the other hand, no measurable decrease in the electron yield for the activated target surface treated at 420°C was obtained within the limit of the experimental errors by the prolonged bombardments of various ions for ten hours.

Discussion

As seen in Figs. 3 and 4, the electron yield of the activated surface treated at 420°C for the argon ions or the various ions of ethylene is considerably larger and more stable than that of the non-activated surface. Moreover, as seen in Figs. 3—6 (excepting the results obtained for the activated surface at 480°C in Fig. 6), the increment of the electron yield for each activated surface with the kinetic energy of various ions in the range 600 to 1000 V. is very small, while that for the non-activated surface in the same energy range is considerably large. The typical results shown in Fig. 6 indicate that the electron yield and the increment of it with the kinetic energy of ions are greatly influenced by the temperature of the treatment. It is worth while to notice that the electron yield curve of the singly-charged neon ions for the target surface activated at 480°C is markedly different from those activated at 350 and 420°C.

These characteristics in the electron yield of the activated target surfaces might be correlated with the structure and the concentration of beryllium oxide formed in the neighborhood of the target surface. But unfortunately, the present results of the electron diffraction analyses shown in Tables I and II can not elucidate the fine structures of the oxide layers, and the more detailed measurements of the surface structure are necessary in order to discuss the correlation mentioned above.

The detailed experiments and theoretical treatise on the mechanism of the electron ejection by the impacts of various noble gas ions from both atomically clean surfaces of molybdenum and tungsten and the surfaces of tungsten covered by various foreign gases have been reported by Hagstrum[5,6]. From his results it has been suggested that the probability of the electron ejection in a non-Auger process may begin at low ion energies when a monolayer is present on the target surface and that even for the atomically clean surface there is strong evidence of a non-Auger process setting in at energies above 400 eV. with the singly-charged helium ions.

The present results shown in Figs. 3—6 indicate that the electron yield for the activated surface of copper-beryllium by various noble gas and hydrocarbon ions is only slightly influenced by the kinetic energy of ions, while for the non-activated target surface there is a marked increase in the electron yield with the increase in the ion kinetic energy. But since we must recall that under the present experimental conditions the considerable part of the target surface might be covered by the residual gases, it seems unreasonable to simply correlate the mechanism of the electron ejection from the activated and non-activated surfaces to the Auger and a non-Auger processes, respectively.

Hagstrum[3] also reported that when the electron ejection from the target surface is mainly dominated by the Auger neutralization process the electron yield is proportional to the value of the ionization potential minus twice the work functions of the target surface. The present results of the electron yield for the target surface activated at 420°C and the literature values[9] of the ionization potentials are summarized in Table III. When we assume that the electron ejection from the activated target surface of copper-beryllium simply obeys the Auger neutralization process and that the work function was unchanged throughout the

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[9] G. C. Eltenton, *J. Chem. Phys.*, 15, 455 (1947).

measurements, it is reasonable to expect that the electron yield is proportional to the ionization potential. Table III indicates that the present results are somewhat complicated and do not simply satisfy the proportionality mentioned above.

Since the present experimental conditions are considerably complicated, it is necessary to continue more detailed experiments on the dependency of the electron yield upon the ion energy and energy distribution of secondary electrons both for the activated and non-activated target surfaces which are atomically clean and covered by foreign gases in order to discuss the mechanism of the electron ejection process.

Summary

The secondary electron emission from the non-activated and activated surfaces of copper-beryllium (4%) by the impacts of various noble gas and hydrocarbon ions was studied together with the determination of the surface structure by the electron diffraction analysis. The main results obtained are as follows.

(1) The considerably thick layer of beryllium oxide is formed in the neighborhood of the target surface activated by oxygen at the temperature range of 350 to 480°C.

(2) The oxide films of copper are formed on the target surface by electropolishing, but these oxides easily undergo reduction by the prolonged ion bombardments.

(3) The optimum temperature of activation for the electron yield seems to be about 420°C, and the electron yield for the activated target surface treated at 350 or 420°C is only slightly dependent upon the ion kinetic energy.

(4) No measurable decrease in the electron yield for the activated surface treated at 420°C was obtained by the prolonged bombardments of various positive ions for ten hours, while the electron yield for the non-activated surface decrease about 20 per cent by the prolonged bombardments of ions for five hours.

(5) Under the present experimental conditions, the mechanism of the electron ejection process seems to be considerably complicated and it is difficult to deduce any definite conclusion for the electron ejection process.

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