The value at 0°K was extrapolated assuming $K_1 = a \times \exp(-bT^2)$.

These results agree with those shown in Fig. 5, within the experimental error. However, the decrease of K_1 with increasing temperature is slightly more rapid according to Bozorth's data than according to mine; his results are best fitted by a fifth-power law, $K_T/K_0 = (M_T/M_0)^5$.

ACKNOWLEDGMENTS

These measurements were undertaken as a result of questions arising from some experiments by R. W. DeBlois and C. P. Bean, whose encouragement and assistance were most helpful. The previous work of J. S. Kouvel in the measurement of anisotropy was of great value, and J. J. Becker made a number of valuable suggestions about the presentation.

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Low-Energy Sputtering Yields in Hg†

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Further data on sputtering yields for normally incident Hg^+—ion bombardment in the energy range of 50 to 400 ev have been collected. Experimental data are used to determine the influence of atomic weight and heat of sublimation of the target material and to establish an empirical sputtering relation. Results provide strong support for a picture of sputtering which might be termed "playing three-dimensional billiards with atoms." The degree of filling of the inner shells, especially the *d* shells, determines how closely collisions approximate hard-sphere collisions. Energy is transferred most efficiently in metals with completely filled *d* shells. Accordingly, Cu, Ag, and Au have the highest sputtering yields. Results for Hg^+—ion bombardment support theories developed by Langberg and by Silsbee but disagree with a theory published by Henschke. Conditions may be different, however, for the case of bombardment with light ions such as hydrogen or helium.

The sputtering yields of alloys do not seem to differ substantially from those of their main constituents.

INTRODUCTION

THE present study is a continuation of previous work on low-energy Hg^+—ion sputtering.[1] The goal is and has been to measure sputtering yields of metals and semiconductors under normally incident Hg^+—ion bombardment primarily as a function of ion energy in the range 50 to 400 ev. Conditions necessary for obtaining reliable results, the measuring procedure, and the apparatus have been described in detail in the earlier paper to which reference should be made.

Targets to be sputtered are immersed in a low-pressure Hg vacuum arc tube like large negative Langmuir probes. Discharge data are as follows: 2.5 amp discharge current, 30 volts discharge voltage drop, Hg gas pressure ~1 micron, ion current density at target ~5 ma/cm², target temperature during sputtering ~400°C. Yields are determined by measuring the weight loss of the target after removal from the demountable tube. Yields are given in $S/(1+\gamma)$ atoms/ion where γ is the electron yield resulting from ion bombardment, a value which is of the order of 0.1 to 0.2 in our energy range.

SPUTTERING YIELD DATA

Titanium.—In recent experiments with Ti somewhat different yields were found than those previously reported. Upon re-examination of the original target material it was discovered that a stainless steel alloy had been measured instead of Ti. The correct curve for Ti is shown in Fig. 1. Occasionally considerably lower than normal yields were found and in these cases we suspected a small leak in the tube. In order to check this point, measurements were made with a controllable leak. It was found, indeed, that small traces of air reduced the sputtering rate of Ti very markedly. In the case of a Ge target, however, the yield was scarcely affected by a leak.

Chromium.—Previous measurements on Cr did not give very consistent results. Recently, samples of ductile Cr were obtained.[2] The yields of this material and of

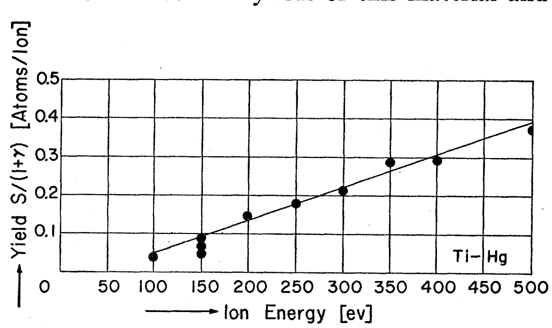

FIG. 1. Sputtering yield of Ti *vs* ion energy.

† This work was performed under contract with the Office of Naval Research.

[1] G. K. Wehner, Phys. Rev. 108, 35 (1957).

[2] Courtesy of Bureau of Mines, Albany, Oregon.

electrolytically prepared Cr samples are compared in Fig. 2.

The reason for the unusually large scattering of the yield points is still unknown.

Be as well as Mn caused unexpected difficulties in that the targets became covered with an unidentified black deposit when sputtered. Rigid outgassing of the targets by electron bombardment before sputtering has not remedied this problem.

It proved to be impossible to collect any reliable sputtering data for boron because of its high electrical resistance. The large voltage drop within the sample makes the actual bombarding energy of the ions rather indeterminable.

Alloys.—The question arose as to whether sputtering yields of alloys differ substantially from those of their constituents.

Figure 3 shows the sputtering rates of some Ni-base alloys, together with the yield curves of the main constituents, Ni and Cu. The yield of Inconel (77% Ni, 15% Cu, 7% Fe) is found to be essentially the same as that of Ni. *K* monel (66% Ni, 29% Cu, 2.7% Al, 0.9% Fe, 0.5% Si) and *S* monel (63% Ni, 30% Cu, 4% Si, 2% Fe) differ only slightly in yield but differ strikingly in their etch patterns developed by ion bombardment. *S* monel reveals pronounced dendritic etch patterns, while *K* monel shows a smooth and fine crystalline surface. The surface contours reveal that the eutectic Cu-rich composition in between the dendritic branches in the S monel is sputtered more rapidly than the Ni-rich solution of the dendritic branches proper.

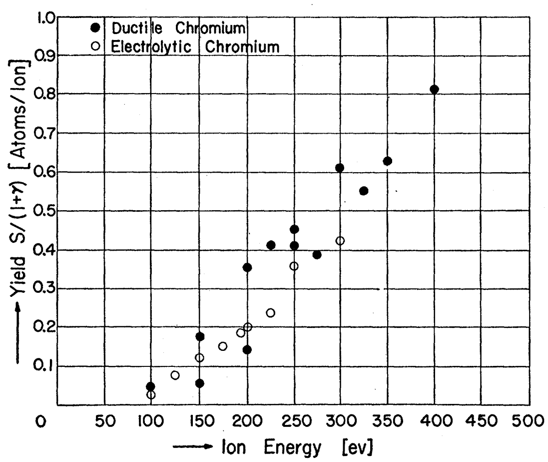

FIG. 2. Sputtering yield of Cr *vs* ion energy.

Figure 4 shows yields for some steels. The yield for stainless steel 303 was found to be somewhat higher than that of pure Fe. The yield of a low-carbon steel (*SAE* 1020 with 99.3% Fe, 0.2% C and 0.5% Mn) was found to be identical with that of pure Fe. Cast iron (97% Fe, 3% C) gives a somewhat lower yield than Fe.

Figure 5 shows some yield values for Al alloys. The yields of Al 319 (90.2% Al, 3.5% Cu, 6.3% Si) and of Al, 356 (92.7% Al, 7% Si, 0.3% Mg) are practically identical with those of Al.

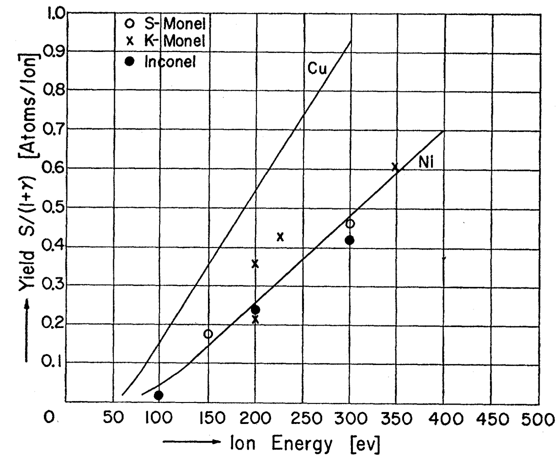

FIG. 3. Sputtering yield of *S* monel, *K* monel, and Inconel *vs* ion energy. Formerly determined Cu and Ni yields are included for comparison.

We measured the yields of austenitic manganese steel, Kovar, and several stellites also. No case was found in which the yields differ substantially from those of the main constituents.

INTERPRETATION OF DATA

Data gathered thus far, although confined to the case of Hg^{+}—ion bombardment, should provide sufficient material to check the influence of those target-material parameters which supposedly play a major role in the sputtering process.

From results to date and from other studies which we are presently undertaking in low-energy sputtering (particularly the study of atom ejection patterns[3]) a general picture of Hg^{+}—ion bombardment sputtering

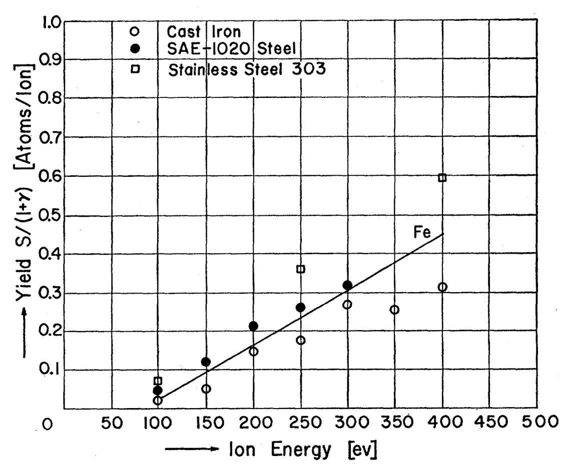

FIG. 4. Sputtering yield of cast iron and two steels *vs* ion energy. Formerly determined yield of pure iron is included for comparison.

[3] G. K. Wehner, J. Appl. Phys. 26, 1056 (1955).

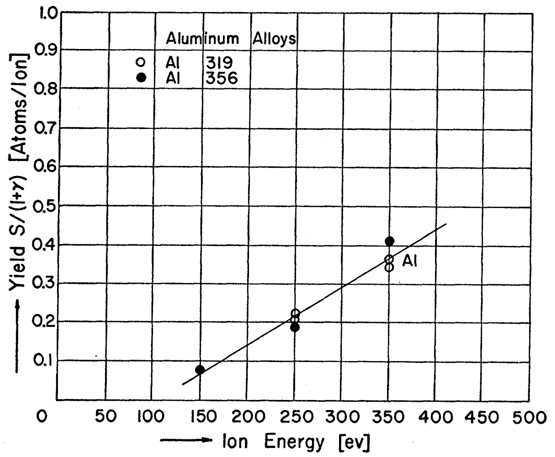

FIG. 5. Sputtering yield for two Al alloys. Formerly determined Al curve is included for comparison.

emerges which might be roughly described as playing three-dimensional billiards with atoms. An ion approaching to within several A of a metal surface first pulls a field-emitted electron from the surface and is neutralized before actually impinging on or entering into the surface. Energy and momentum are transferred from the neutralized ion to a first target atom in a collision which more or less resembles a hard-sphere collision. This target atom then transfers energy to other close neighbors and, finally, a small amount of the original energy, with a momentum directed to the outside, may separate a surface atom from the lattice in the neighborhood of the place of impact. Only a relatively few atoms near the place of impact become involved in the sputtering process.

The fact that the energy is transferred much more efficiently along the closely packed directions of the crystal lattice than in other directions gives rise to strongly anisotropic effects which are responsible for the ejection patterns observed in single-crystal sputtering.

One can simulate heavy-particle, low-energy sputtering quite adequately with the following model. Approximately 100 steel spheres are suspended by thin wires from the ceiling in such a way that they form a closely packed plane [fcc (111) plane], which represents the metal lattice reduced by one dimension. When one of the edge spheres in this assembly is moved some distance away and then released, the sphere bounces against the edge of the sphere assembly representing the target surface. At high kinetic energy one observes that in this collision process some spheres may be ejected at the far end of the assembly. At low kinetic energy visible effects are confined to the vicinity of the place of impact and "atoms" are ejected or "sputtered" with momentum reversal from the surface. The directions of ejections are in close neighbor directions, exactly as in actual sputtering.

At very low ion energy, i.e., near the "cut-in" energy, formerly called "threshold energy," only the most favorable collisions may yield a sputtered atom. This case has been studied theoretically by Langberg.[4] The minimum number of atoms necessary for momentum reversal constitutes the case in which only the neutralized ion and two target atoms become involved. The two collisions between the three particles are treated as consecutive binary collisions between free particles with the interatomic forces determined by a Morse potential function. The "cut-in" energy values determined from this theory (without adjustable parameters) are in the general range of the experimentally determined values.

Two papers on low-ion-energy sputtering analysis have recently been published by Henschke.[5] Henschke assumes that under normal incidence the ion first collides with a lower surface atom, then rebounds and strikes an upper surface atom from below in such a way that it is separated from the surface. In order to explain certain details in the atom ejection patterns, Henschke had to assume double rebounding collisions in some

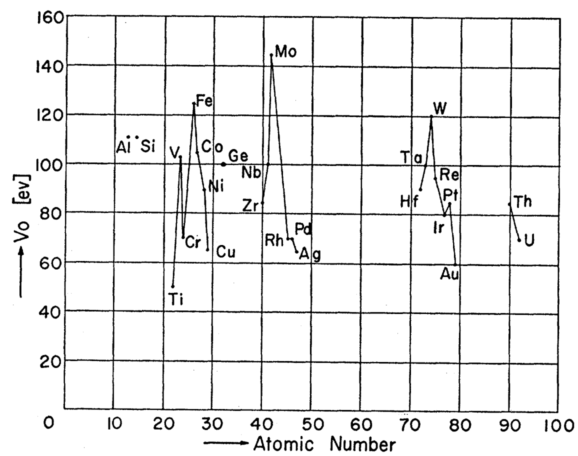

FIG. 6. "Cut-in" energies *vs* atomic number.

cases. It is difficult to understand, however, how a heavy neutralized ion such as that of Hg could rebound from lighter target atoms in a head-on collision, or why a target atom, together with its neighbors, should act like a solid wall, as Henschke describes it. Such conditions would require that the first collision still be in progress after other neighboring target atoms have already been brought strongly into play. Theoretical as well as experimental evidence exists which indicates this is not the case here. Langberg has calculated conditions for a Morse potential interaction in our energy range and finds that the collisions can be treated with good approximation as subsequent binary collisions just as in a hard-sphere model with the spheres somewhat separated from each other. In recent experimental studies of forces on ion-bombarded surfaces and of accommoda-

[4] E. Langberg, Phys. Rev. **111**, 91 (1958).
[5] E. B. Henschke, J. Appl. Phys. **28**, 411 (1957), and Phys. Rev. **106**, 737 (1957).

tion coefficients for Hg^+—ions,[6] we found that the number of rebounding neutralized Hg^+—ions is extremely small. Hg^+—ions are completely accommodated on Cu, Ag, and Au surfaces, i.e., on those metals which have completely filled *d* shells and which behave most closely like a hard-sphere model. In Henschke's sputtering model one should expect that Cu, Ag, and Au would exhibit low sputtering yields. The opposite is the case, however. Cu, Ag, and Au have the highest yields found thus far, obviously because energy is transferred most efficiently from atom to atom in the case of the "hardest" atoms. A process such as described by Henschke is possible only when light ions bombard heavy target materials.

At ion energies above "cut-in" energies, i.e., several hundred ev, more than two collisions may be involved in the sputtering process and a theoretical treatment becomes complex. A further difficulty in an exact treatment arises from the fact that in subsequent collisions

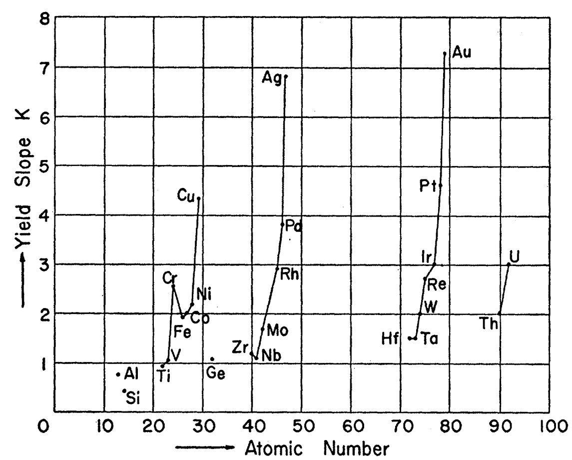

FIG. 7. Yield slopes *vs* atomic number.

with progressive dilution in energy the atoms behave like larger and larger spheres.[7]

An attempt is made below to establish from experimental data the influence of certain parameters and to uncover empirical relationships by studying the periodicity of "cut-in" energies and yield slopes within the periodic system of the elements.

The yield curves have, in general, a form $S=k(V_i-V_0)$, where S=sputtering yield [atoms/ion], k=slope [ev^{-1}], V_i=ion energy [ev], and V_0="cut-in" energy [ev]. Figure 6 shows "cut-in" energies and Fig. 7 the slopes plotted as a function of the atomic number of the target material. The data are for normally incident Hg^+—ion bombardment and represent the latest and most reliable data from our previous and present work.

[6] G. K. Wehner, Conference Report, Massachusetts Institute of Technology Conference on Physical Electronics, 1958 (unpublished).

[7] R. H. Silsbee, J. Appl. Phys. 28, 1246 (1957).

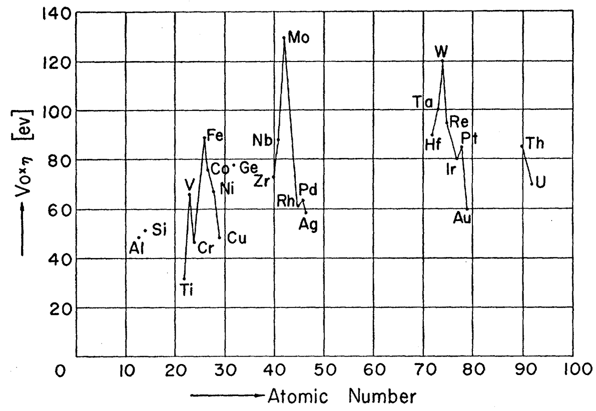

FIG. 8. Normalized "cut-in" energies *vs* atomic number.

The following general features emerge from these graphs. The "cut-in" energies have maxima for metals like Fe, Mo, and W. Comparing values from different periods, one finds a slight tendency for values to decrease with increasing atomic weight. From the billiard model of sputtering, one should expect that the energy transfer from the ion with mass m_1 to the target atom m_2 would enter into the picture. Normalized "cut-in" energies, i.e., energy transferred in a central elastic collision to a target atom, $V_0\times\eta$, where $\eta=4m_1m_2/(m_1+m_2)^2$, are plotted in Fig. 8. This graph bears a definite resemblance to a plot of the heats of sublimation (H) as shown in Fig. 9. A closer comparison of the two curves shows that the "cut-in" energies of metals which have a close-packed hexagonal structure, such as Ti, Co, Zr, Hf, and Re, seem to be on the low side, possibly indicating that conditions for low-energy sputtering are more favorable in this atomic arrangement.

The conclusion to be drawn is that the "cut-in" energies of different metals are in a first approximation proportional to H/η, with the dimensionless proportion-

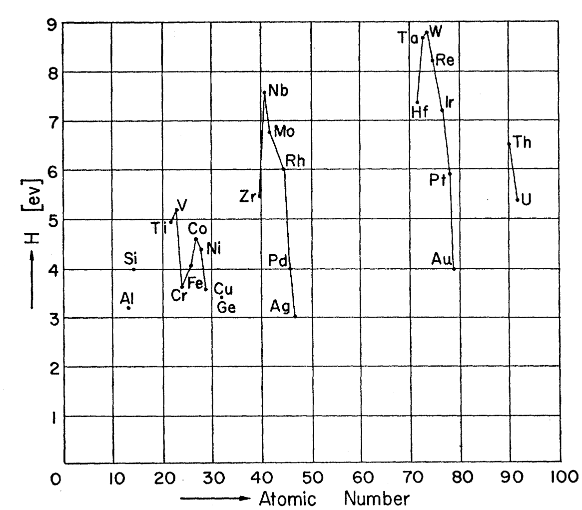

FIG. 9. Heats of sublimation *vs* atomic number.

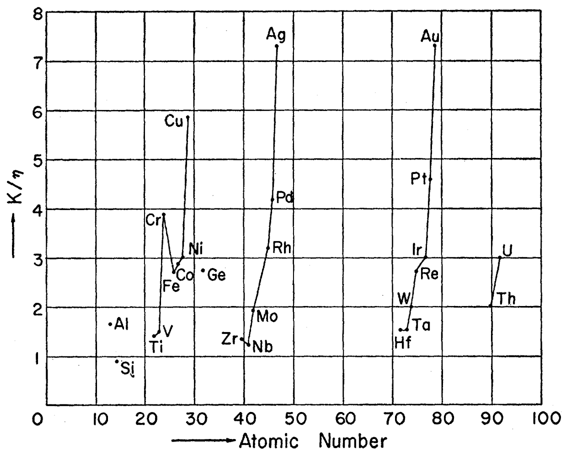

FIG. 10. Normalized yield slopes *vs* atomic number.

ality factor between 8 and 20 which can be compared favorably with Langberg's calculated value of 14.

Figure 7 shows that the trend for yield slopes is quite different from that of the "cut-in" energies. Slopes within the different periods rise, with Cu, Ag, and Au yielding the highest values. Comparing yield slopes from different periods, one notes that values rise with increasing atomic weight. The slopes can be normalized, or different periods can be brought to the same general level, by dividing experimentally found values by η. The normalized slopes, shown in Fig. 10, appear to be unrelated either to crystal structure or to heats of sublimation. The determining factor seems to be the degree to which the inner electronic shells are filled. In the fourth period the $3d$ shell contains two electrons in Ti and becomes complete with 10 electrons in Cu. In the fifth period the same situation exists in the $4d$ shell with Zr (2) to Ag (10) and again in the sixth period with the $5d$ shell becoming increasingly filled from Hf (2) to Au (10). The fact that yield slopes rise in conformity with the degree of filling of the d shells obviously indicates that the collisions increasingly approximate hard-sphere collisions. This result checks well with results recently obtained in our studies of forces on ion-bombarded electrodes; accommodation coefficients for Hg^+—ions on metal surfaces approach unity or, in other words, energy transfer to the metal lattice is accomplished more efficiently with increased filling of shells. Heats of sublimation, surprisingly, have hardly any influence on yield slopes. It is of interest to mention here that recent measurements of the average kinetic energy of sputtered atoms gave values several times higher than the heats of sublimation.[6]

The conclusions to be drawn are that the yield curve slopes are proportional to the energy transfer factor η and a function of the "hardness" of the atoms. The harder the collision, the better the energy transfer to and within the lattice and the steeper the rise of the yield. The difference between "hard" metal atoms like Cu, Ag, and Au and "soft" atoms like Zr, Ti, and Hf changes yield slopes by a factor of $\sim$5. "Cut-in" energies are less directly related to the hardness of the atoms, probably because of the small number of collisions involved in this case. Here, however, crystal structure and atomic arrangement at the surface may play a more dominant role.

We are at present collecting yield data in rare gases and hope soon to report to what degree the picture presented above holds for Xe^+—ion bombardment and to what degree this picture must be modified in the case of a light ion like He^+ bombarding a heavy target metal.

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Mr. Benjamin Meckel and Mr. Roger Moseson made the measurements with great skill and contributed many ideas. Mr. Emil Benz and Mr. Arthur Haut did an excellent job on all the glass work.