The Stewart-Thompson Theory applied to the Glow Discharge

P. A. Büger, F. Blum, and J. H. Schilling

National Physical Research Laboratory, C.S.I.R., P.O. Box 395, Pretoria, 0001 South Africa

Z. Naturforsch. **33a**, 321–326 (1978); received September 16, 1977

The surface topography developed on copper-based and ferrous alloys after being sputtered in a glow discharge lamp and in an ion microprobe was studied by means of a scanning electron microscope and an ion microprobe mass analyser. The observed surface topography, though obtained under completely different conditions, was found to be similar to that predicted by the theory of Stewart and Thompson.

1. Introduction

The removal of material from a solid target bombarded by ions and atoms in a glow discharge is explained by the collision model [1, 2]. The basic concept of this model is that kinetic energy is transferred by the primary ions to the lattice atoms of the bombarded sample. Some of this initial energy returns to the surface and consequently surface material is released.

A surface topography develops during the sputtering process revealing cones as well as recessed areas [3]. The formation of these particularities on the sputtered sample surface has been related to the dependence of the sputtering ratio on the angle of incidence [4] and resulted in the theory of Stewart and Thompson. This theory has been confirmed by several authors [5, 6]. In the reported cases single crystals of pure metals were bombarded by a rather monoenergetic ion beam under a uniform angle of incidence, whereas in the case of the glow discharge the targets were alloys and the discharge conditions were quite different (see Table 1).

Table 1. Comparison of the working conditions used in the sputtering experiments by means of the glow discharge lamp and the ion microprobe mass analyser and those used in the experiments reported by Stewart and Thompson [4].

	GDL	IMMA	Ref. [4]
working pressure (Pa)	500	10^{-4}	10^{-3}
bomdarding species	Ar^+, Ar, particles from target	Ar^+	Ar^+
energy of bombarding species (keV)	0.1	20	5–8
current density ($\mu A\ cm^{-2}$)	$2 \cdot 10^5$	6	300

Reprint requests to Dr. J. H. Schilling, National Physical Research Laboratory, C.S.I.R., P.O. Box 395, Pretoria/0001, South Africa.

The aim of the present paper is to investigate empirically the surface topography developed during ion bombardment in a glow discharge lamp and to bring it into relation to the theory on cone formation by Stewart and Thompson. The alloys selected are representative of samples which are often analysed in glow discharge lamps.

2. Experimental

Commercially available copper-based and ferrous alloys, which were mechanically ground and polished, were subjected to Ar^+ bombardment in a glow discharge lamp (GDL) and in an ion microprobe mass analyser (IMMA) [7]. The discharge conditions as listed in Table 1 were similar to those normally used for spectrochemical analysis of this type of sample.

The sputtered samples were then examined by means of a scanning electron microscope (SEM) which was equipped with an energy dispersive X-ray (EDX) spectrometer. Scanning electron micrographs and X-ray spectra were recorded from typical surface areas. Supplementary information, especially the determination of light elements, was obtained by studying the samples with the IMMA as well. For this purpose oxygen $^{16}O_2^+$ was chosen as bombarding species, which does not result in the development of surface topography as caused by argon bombardment [8].

3. Results

Figure 1 is a secondary electron micrograph of a typical sputtered area of a Cr^{18}-Ni^{10} stainless steel sample (SRM 1152, containing amongst other elements about 18,49 wt.% Cr, 10,21 wt.% Ni, 0,12 wt.% Ti, 0,163 wt.% Mn and 0,2 wt.% Nb). The machined sample surface was exposed to

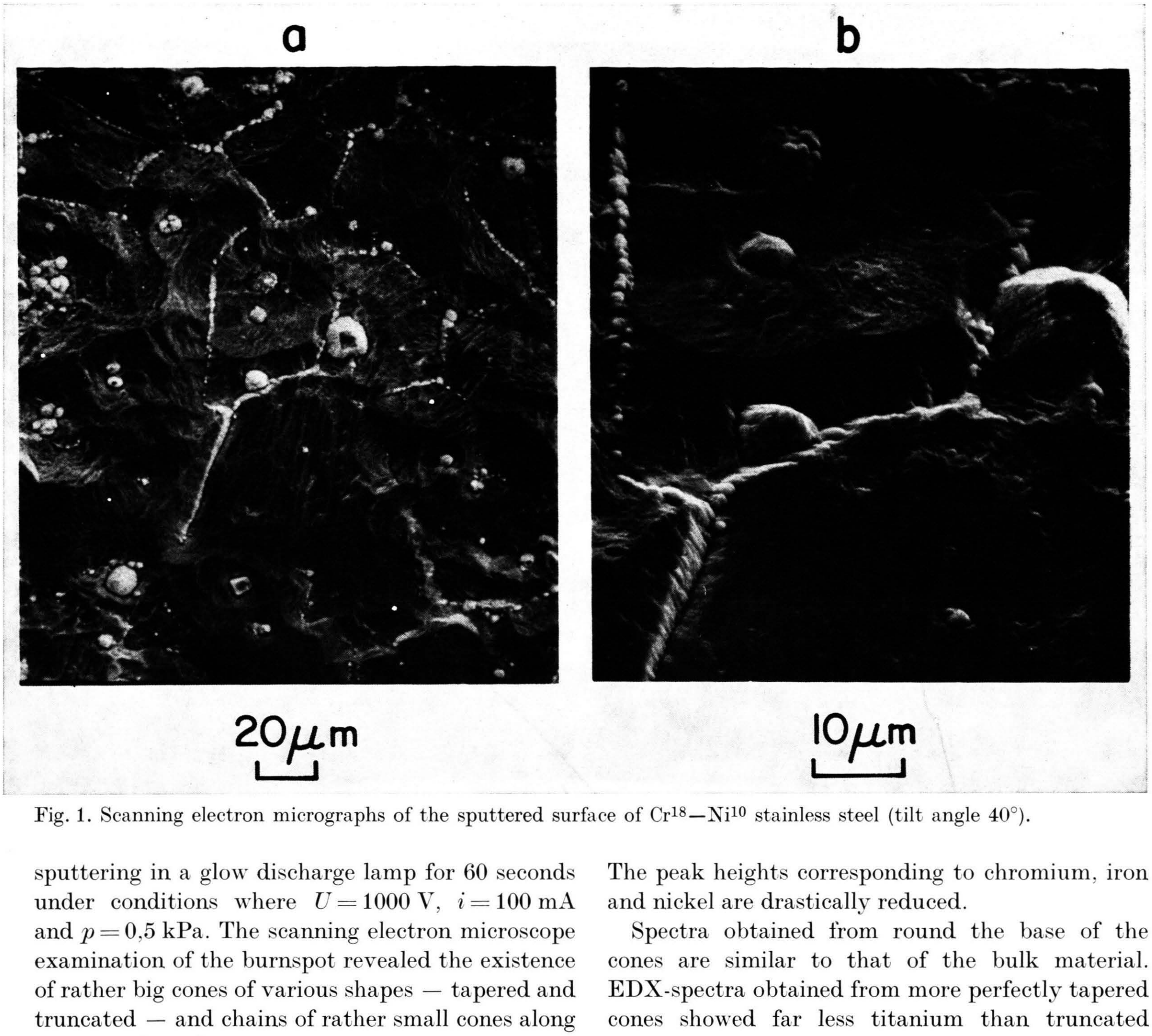

Fig. 1. Scanning electron micrographs of the sputtered surface of Cr^{18}—Ni^{10} stainless steel (tilt angle 40°).

sputtering in a glow discharge lamp for 60 seconds under conditions where $U = 1000$ V, $i = 100$ mA and $p = 0{,}5$ kPa. The scanning electron microscope examination of the burnspot revealed the existence of rather big cones of various shapes — tapered and truncated — and chains of rather small cones along the grain boundaries.

Figure 2 shows one of the truncated cones at higher magnification and two EDX-spectra. Spectrum (a) was obtained by scanning an unsputtered area of about 0,5 mm^2 and is representative of the chemical composition of the steel. Only chromium, iron and nickel can be detected as seen from the intensity peaks corresponding to the $K\alpha$-radiation at 5,4 keV, 6,4 keV and 7,4 keV, respectively. The peaks at 5,9 keV and 7,06 keV are due to the $K\beta$-radiation of chromium and iron. Spectrum (b) presents the results of a microanalysis of the top of the cone. The intensity peaks at 4,5 keV and 4,9 keV correspond to X-radiation of titanium, which could not be detected from the bulk analysis. The peak heights corresponding to chromium, iron and nickel are drastically reduced.

Spectra obtained from round the base of the cones are similar to that of the bulk material. EDX-spectra obtained from more perfectly tapered cones showed far less titanium than truncated cones and it was found that the more perfectly the cone was shaped the smaller the peak recorded for titanium was.

Microanalyses performed on the chains of cones, which were found along the grain boundaries, were not significantly different from those resulting from the bulk analysis. IMMA examination of these parts revealed a significant enrichment of carbon along these chains of small cones.

When changing the sputtering time, with all the other discharge parameters kept constant, the following observations were made: Up to a sputtering time of 20 seconds (total dose of 4 C/cm^2) only the grain boundary areas are attacked and no pronounced surface topography has developed.

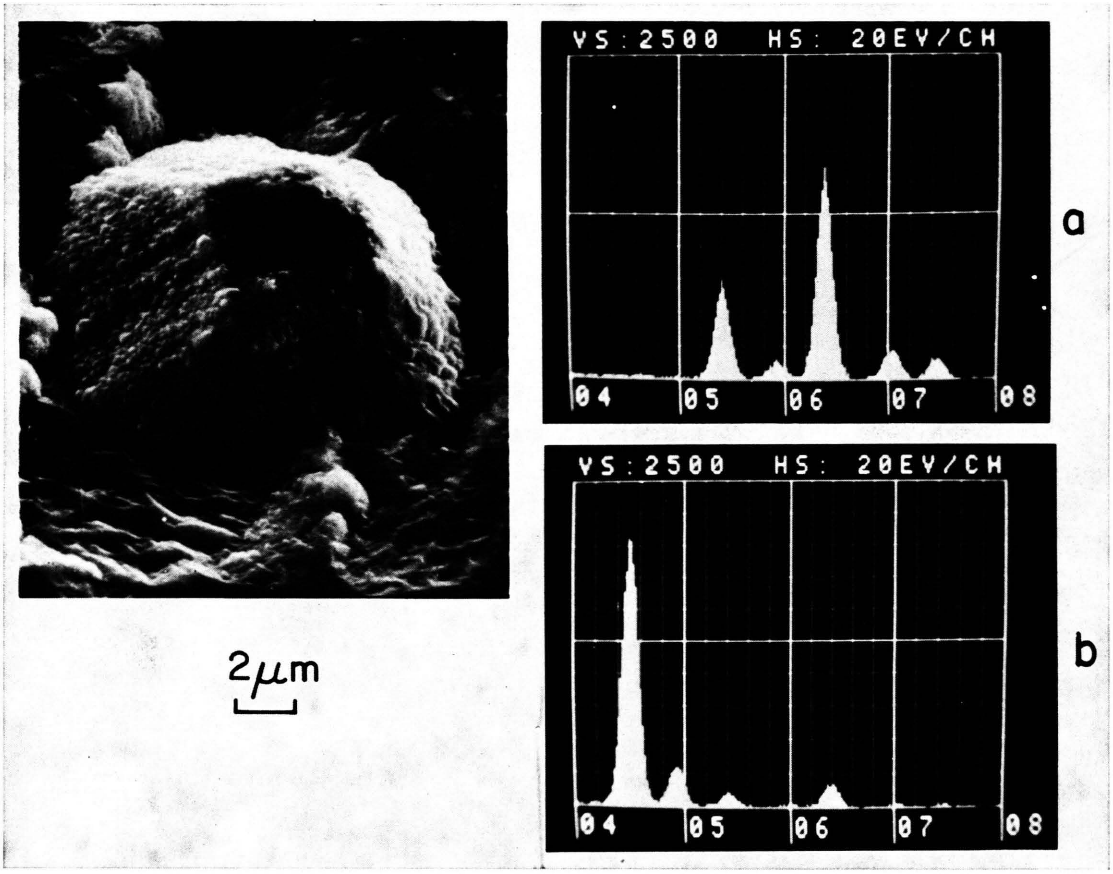

Fig. 2. Scanning electron micrograph of a cone developed on a Cr^{18}—Ni^{10} stainless steel. X-ray spectra as aresult of microanalysis of an unsputtered area (a) and microanalysis of the top of the cone (b). Vertical scale: total counts. Horizontal scale: X-ray energy (keV) calibrated in channels of 20 eV per channel.

An increase in sputtering time to 25 seconds results in the first appearance of some hillocks. The first flat cones, enriched in sulphur and manganese, appear after the sample had been sputtered for 35 seconds (dose of 7 C/cm^2). A surface topography revealing mainly truncated cones, as depicted in Fig. 1, can be observed after a sputtering time of 50 seconds. Titanium and niobium were detected at the top of most of the cones. A further increase in sputtering time changes the developed surface topography to the extent that truncated as well as tapered cones appear.

Figure 3 illustrates a typical sputtered area of a copper-based alloy exposed to sputtering in a GDL (3a) and in an IMMA (Fig. 3b). The differences in cone structure, the size of the cones (note different magnifications) and the number of cones spread over the investigated area can be seen immediately. Cones developed in the GDL show a Pb enrichment at the top, while for the cones developed in the IMMA no elemental enrichment could be detected.

4. Discussion

The formation of cones on the sample surface exposed to sputtering in a GDL seems to be linked to the presence of foreign particles in the matrix (lead in the copper alloy [3]; niobium and titanium in the steel). The stages of formation of such a cone and the observation that truncated cones show a strong signal from the element present as inclusion (Pb, Ti, Nb) while the signal decreases with advanced perfection of the cone, are in accordance with the theory of Stewart and Thompson.

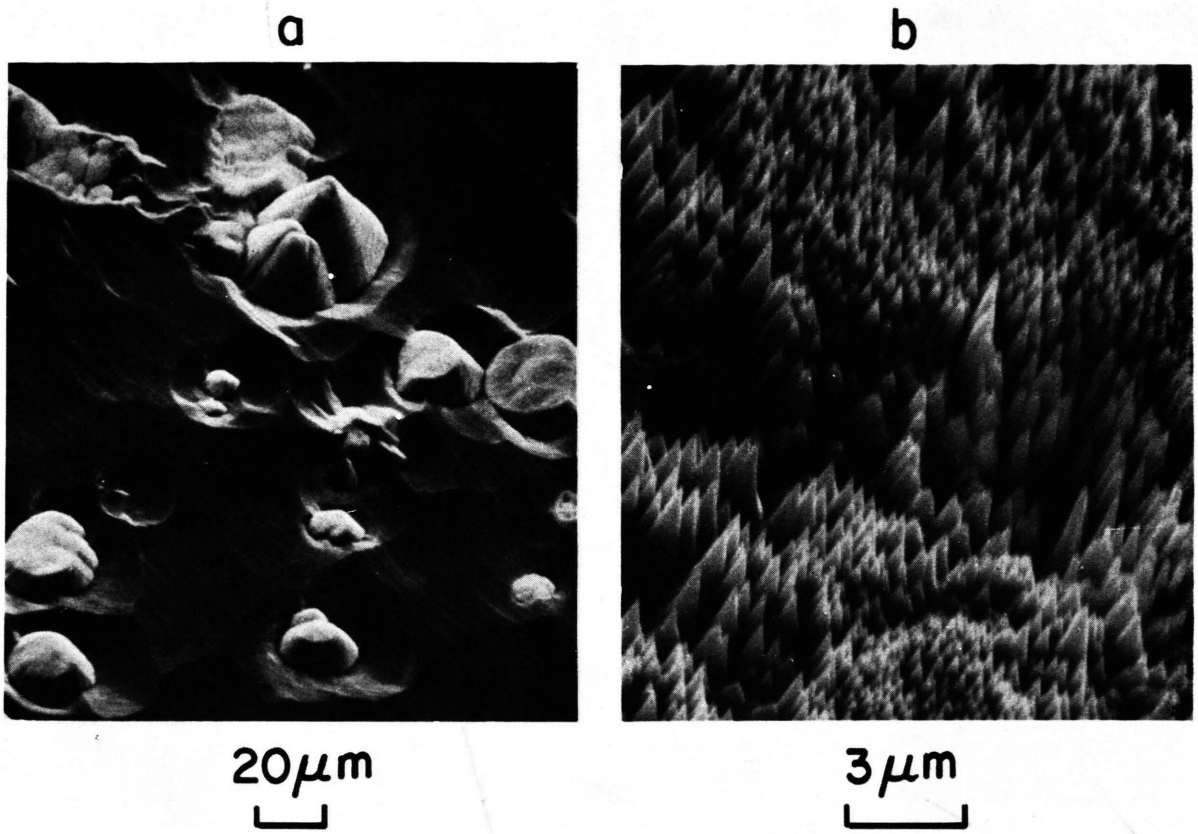

Fig. 3. Scanning electron micrograph of tilted surface of a copper-based alloy, exposed to sputtering in the glow discharge lamp (a) and in the ion microprobe mass analyser (b).

On the other hand, on the basis of this theory, cones can only form under the impact of a rather monoenergetic ion beam with a small angular distribution. The theory predicts that after the formation of a small surface step, induced by a foreign particle such as an inclusion, the dependence of the sputter ratio on the angle of incidence causes the formation of cones. The sputter ratio increases when the angle between the incident ion and the normal of the bombarded surface is increased and decreases again after passing a maximum of an angle, typically 70—80°, referred to as the angle for optimum sputtering [4]. This theory applies, according to Stewart and Thompson, when samples of pure crystals (metals) are bombarded by 5—8 keV argon ions.

The conditions in a glow discharge for the ion bombardment are completely different and the possibility of obtaining a monoenergetic ion beam with a small angular distribution seems to be rather small. The working pressure is high, therefore the bombarding species have to undergo some collisions before they strike the target. Also the cross-section for a charge transfer process ($Ar^+ + Ar \rightarrow Ar + Ar^+$) is high. Based on these two facts no argon ions created in the negative glow and having the full available energy of the cathode fall will strike the target. According to Denk [9] most of the bombarding ions have very low energies and the number of ions having energies in excess of 100 eV is already negligible.

The question [9] of whether ions or atoms are bombarding the surface of the sample causing the sputtering process does not change the considerations because no significant difference in sputtering between ions and atoms is expected. The ion must be neutralized at the surface, therefore some extra energy is necessary and must be available to release an electron. This extra energy can play a role only when very low energies close to the threshold energy are present.

We now have to consider ions with low energies close to the threshold and a relatively large energy spread. Ions with low energies cannot penetrate deeply into the target and the penetration will not go far beyond one monolayer. Therefore, a sputtering mechanism different from the one where high energy particles (IMMA: 20 keV; Ref. [4]: 5–8 keV) penetrate deeply into the lattice (IMMA: ≈ 12 nm; Ref. [4]: ≈ 5 nm) must also be considered. High energy particles cause a cascade of collisions in the direction of the lattice whereby the momentum transferred is spread over a wide angle and will finally have a component which points outwards from the lattice, transferring enough energy to a surface atom to be released. Slow particles with energies near the threshold also knock the first hit atom into the solid bulk. In one or two collisions this atom must be reflected backwards to the surface in order to release a surface atom.

High energy particles are supposed to penetrate deeply into the lattice but there is a possibility that the reflected momentum may not carry enough energy to release a surface atom, or it may not reach the surface at all. Bombardment at an angle increases the probability for releasing an atom because the particles do not penetrate so deeply into the material. Therefore, the dependence of the sputter ratio on this angle is pronounced for elements with low sputter rates (a relatively large ratio of energy is necessary to release a surface atom) and is reduced for bombarding particles with lower energies.

Therefore, when ions with low or very low energies are used in a GDL the importance of the basic considerations of the theory is considerably reduced. The angle of incidence being most important to obtain optimum sputtering in the work reported [4–6] is now much less important and therefore the application of the Stewart and Thompson theory in the case of the glow discharge seems inappropriate.

If the applicability of the theory is accepted in the case of the ion bombardment in the IMMA, where the conditions are rather similar to Ref. [4], it is also evident when comparing picture 3a

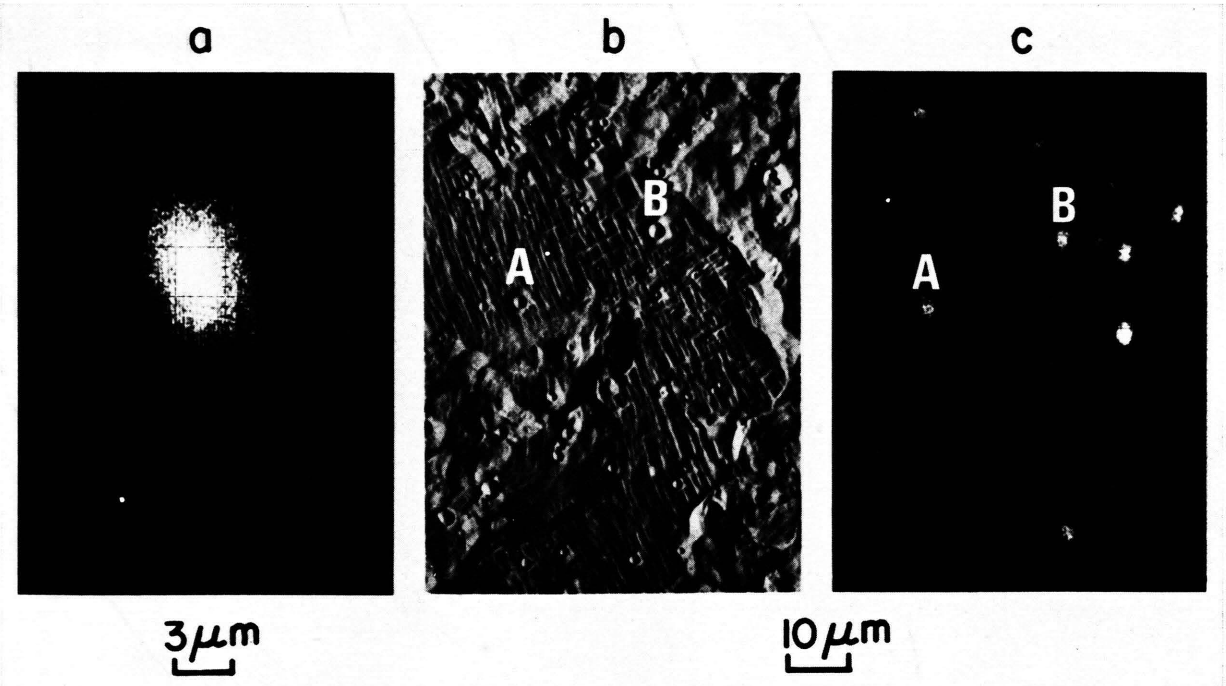

Fig. 4. Elemental image depicting titanium content of an inclusion (a), scanning electron micrograph showing the topography of a sputtered area including cones (b) and elemental image of titanium as obtained in the IMMA showing the same area (c). A and B are inclusions which cause the formation of cones.

and 3b that a different mechanism must be responsible for the formation of cones in a GDL.

On closer inspection of an inclusion (Fig. 4a) suspected of causing the formation of cones, it was found that the inclusion consists of a core and some kind of coating. Analysis with the IMMA showed that the inclusion is mainly composed of titanium (about 90%), with carbon, manganese and sulphur also present in higher concentrations. The inclusions can be positioned in any direction, concentration profiling showing differences in core and coating are very difficult, but it seems that in most cases MnS is found in the coating.

If such an inclusion is considered to be the cause of the formation of a cone, a truncated cone is expected to be found at each inclusion producing a significant signal for titanium. According to Figs. 4b and 4c, which show a scanning electron micrograph of a sputtered area and an elemental image of titanium as obtained by the IMMA of the same area, it can be seen that only in some cases precipitates seem to cause the formation of cones. This means that the presence of titanium alone is not the only cause of cone formation, but that certain favourable conditions must prevail, probably such as orientation and size of the inclusion for achieving the biggest differences in the sputter rate resulting in a big surface step. The current density in the GDL is extremely high compared with the one of the IMMA and of Ref. [4], therefore smaller surface steps, induced by the other inclusions, are sputtered away before a cone can form.

5. Conclusion

The surface topography developed on copper and ferrous alloys after being exposed to sputtering in a glow discharge lamp was found to be similar to that predicted in the theory given by Stewart and Thompson even though it should not be applicable. The bombarding conditions in the glow discharge lamp are completely different from those applied in IMMA and Reference [4]. High energy particles penetrate deeply into the lattice in the latter cases, while in the case of the glow discharge particles of rather low energies close to the threshold bombard the sample. In the GDL the angle of incidence of the primary particles being most important for achieving optimum sputtering loses its importance and the whole theory seems not to be meaningful in the case of the glow discharge.

[1] F. Keywell, Phys. Rev. **27**, 1611 (1955).
[2] P. K. Rol, J. M. Fluit, and J. Kistenmaker, Physica **26**, 1009 (1960).
[3] F. Blum, P. A. Büger, and R. J. Murphy, Z. Naturforsch. **30a**, 1247 (1975).
[4] A. D. G. Stewart and M. W. Thompson, J. Mater. Sci. **4**, 56 (1969).
[5] J. H. Wilson and M. W. Kidd, J. Mater. Sci. **6**, 1352 (1971).
[6] Kouzou Tsunoyama, Toshiko Suzuki, and Yoshiharu Ohashi, Jap. J. Appl. Phys. **15**, 349 (1976).
[7] H. Liebl, J. Appl. Phys. **38**, 5277 (1967).
[8] P. A. Büger, F. Blum, and J. H. Schilling, Z. Naturforsch. **32a**, 144 (1977).
[9] H. J. Denk, Dissertation, Düsseldorf 1975.