JOURNAL OF MATERIALS SCIENCE 19 (1984) 2845–2854

Investigation of the surface morphology of ion-bombarded biocompatible materials with a SEM and profilograph

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The surface morphology (topography and roughness) is a very important factor which affects the response of biological tissue to an implant material. The effect of an incident ion beam on surface morphology of various biocompatible materials was studied. All materials were bombarded by Ar^+ ions at an applied voltage of 7 kV at various incident angles from 0 to 1.4 rad (0 to 80°) and at a beam current up to 0.1 mA. The surface topographies of ion-bombarded samples were examined with a Japan Electron Optics Laboratory, model JSM-35, scanning electron microscope. The roughness of the surface was calculated from the shape of a surface profile, which was recorded by a profilograph, the ME10 (supplied by VEB Carl Zeiss, Jena).

1. Introduction

It is well known that ion sputtering of solids may lead to modifications of the surface morphology of these materials. This is a very important feature of the process which gives ion sputtering a new area of potential application in the field of medicine, particularly in implantology. Results of many experiments have indicated that the surface morphology (topography and roughness) is a very important factor which affects the response of biological tissue to an implant material [1–4]. Ion beam sputtering is potentially useful in the study of the effect of surface morphology on the biological response because of the ability of this technique to control the surface topography (and roughness). To obtain suitable surface roughness or controlled surface topography of biomaterials and/or biocompatible materials, three different ion-sputtering techniques can be used [5]:

(a) Natural sputtering (properly: natural texturing, NTex, i.e. microroughening of the ion-irradiated surface of the sample that occurs if there are spatial variations in the sputtering yield of the target surface).

(b) Sputtering with the sputter resistant material, seed material, supplying surfaces during the ion sputtering process, i.e. seed texturing, STex [6, 7].

(c) Sputtering through a screen mesh mask superimposed on the material during ion sputtering. The screen prevents the erosion of the material directly beneath it, resulting in a surface with an array of pores of constant dimension. This technique could be termed pattern texturing, PTex [5].

Using one of the ion texturing techniques described above it is possible to modify the surface morphology of various biomaterials, such as metals, alloys, ceramics and polymers [4, 8, 9]. It is worth noting that seed texturing and pattern texturing techniques have one important fault. Associated with both techniques is some contamination of the target material by the seed or mesh material. Further etching and aqua regia acid bathing appear to eliminate much of the seed and mesh atoms but a small fraction usually remains entrapped. To avoid a contamination problem one should use the first ion texturing technique, i.e., natural texturing, NTex.

The surface morphology caused by ion bombardment is influenced by a great many parameters. Type, energy, and angle of incidence of

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the incoming ions, type of target atoms, crystal structure, surface cleanliness and temperature of the target, dose and duration are among the main parameters. To modifiy the surface morphology of biomaterials and/or biocompatible materials it is profitable to use the first texturing technique, i.e. natural texturing, and various parameters of the ion bombardment process. One important parameter of ion sputtering which affects the surface topography and roughness is the angle of ion incidence.

A major aim of the present study was to determine the influence of the angle of ion incidence on the surface topography of various biocompatible materials. A second objective was to examine the surface roughness as a function of the angle in question.

TABLE I Sputtering yields and etch rates of the biocompatible materials used

Material	Material symbol	Sputtering yield (atom ion^{-1})	Etch rate‡ (A min^{-1})
Stainless steel	304	–	250
Titanium	Ti	0.51*	320
Tantalum	Ta	0.57*	380
Alumina	Al_2O_3	0.18†	100

*Sputtering yields of the materials at 500 eV argon ions energy are from G. Carter and J. S. Colligon, "Ion Bombardment of Solids" (H.E.B. Ltd, London, 1969) p. 323.
†See "Vacuum Manual", edited by L. Holland, W. Steckelmacher and J. Yarwood (E. and F.N. Spon, London, 1974) p. 390.
‡Etch rates of the materials in question for 500 eV argon ions at 1 mA cm^{-2} and normal beam incidence are from 1979 Veeco Catalog, p. T22, Table I. Further information, see [12].

2. Experimental procedure

2.1. Specimens

Four types of samples have been investigated: (a) samples of materials for implanation into the human body now in use, such as chrome-nickel stainless steel and titanium; (b) samples of materials usually applied as seed material in ion texturing processes – tantalum; and (c) samples of material under consideration for implant devices – alumina ceramic.

Chrome-nickel stainless steel samples were cut from a wide plate of type 63018 (Catalogue of OSTEO AG, Selzach products, 1976). This material, used for orthopaedic implants, corresponds to the American standard AISI 316 LC or the German material number 4435.

Titanium is a material utilized for dental implants (titanium endosteel blade vent implants [1]). In the experiment polycrystalline 99.9% titanium was studied. Samples of this material were cut from thin sheets about 0.5 mm in thickness.

Tantalum, most often utilized as seed material [1, 10, 11] in ion texturing of various materials (especially biomaterials) was also studied. Samples of polycrystalline 99% tantalum were cut from rolled sheet at a thickness of about 0.1 mm.

Alumina ceramic is commonly used as a substrate material for thick film circuits but it appeared that it might be a satisfactory biomaterial. Therefore polycrystalline ceramic specimens of mechanically polished 99.5% alumina were also investigated

All four materials investigated are rather low-sputter yield materials. They are sputtered with difficulty and therefore they can be used as seed materials. Table I presents sputtering yields and etch rates of the materials studied.

2.2. Irradiation

The ion bombardment was performed in an experimental apparatus similar to that described elsewhere [13]. The glow discharge ion gun with hollow anode was used as a neutralized ion beam sputtering source [14, 15]. All materials studied were bombarded by Ar^+ ions at an applied voltage of 7 kV and at a beam current, measured by a Faraday cage and flat collector, of up to 0.1 mA. The samples were positioned and ion sputtered for between 2 and 4 h at an ion source–sample distance of about 1.5 cm. Throughout the sputtering processes the operating pressure was between 4.5×10^{-3} and 13.6×10^{-3} Pa (3.5×10^{-5} and 10.5×10^{-5} torr). The ion bombardment conditions and sample numbers for suitable ion incidence angles are presented in Table II.

2.3. Examination of surface topography and roughness

All the samples of the materials studied were examined using a Japan Electron Optics Laboratory, model JSM-35, scanning electron microscope. To avoid surface charging of non-conductive material during SEM observation the alumina samples were coated with a thin film of chromium. Another area of interest was the surface roughness. This is a very important parameter, which must be considered in biological implant materials. The

TABLE II Summary of ion bombardment conditions used to modify the surface morphology of various biocompatible materials

Material	Sample number for beam incidence angle of: 0 (0°)	~ 0.78 rad (45°)	~ 1.05 rad (60°)	~ 1.22 rad (70°)	~ 1.4 rad (80°)	Duration (h)	Source (mA)	Operating (× 10^{-3} Pa)
Stainless steel	1	2	3	4	–	4	0.5	4.5–5.2
Titanium	6	7	8	9	10	4	0.5	5.2–7.8
Tantalum	11	12	13	14	15	2	0.75	–
Alumina	16	17	18	19	20	2	1.0	9.7–13.6

roughness was calculated from the shape of the surface profile recorded by the profilograph, the ME 10 (supplied by VEB Carl Zeiss, Jena).

3. Results

Four samples of chrome-nickel stainless steel were ion beam irradiated at various ion beam incidence angles from 0 to 1.22 rad (0° to 70°). Scanning electron photomicrographs of the sputtered materials are shown in Fig. 1. The ion sputtering process drastically changes the surface morphology of stainless steel. The surface, smooth before ion irradiation, is modified with a tendency towards roughening. Many pits, craters, steps and other topographical features can be observed (Fig. 1a) on the surface after normal (perpendicular) ion beam bombardment. The surface of the sample sputtered at about 0.78 rad (45°; see Fig. 1b) differs from that sputtered perpendicularly. Craters, "column- and/or cone-like" structures are predominant. In isolated areas etch lines can also be seen. All topographical features are oriented along the tangential component of the ion beam. The surface topography of the samples irradiated at near-glancing incidence is very similar. Figs. 1c and d present surfaces of stainless steel after ion bombardment at about 1.05 rad (60°) and 1.22 rad (70°) respectively. All features, i.e. etch lines, grooves, ridges, and "scale-like" structure (or topography) are oriented along the ion beam direction.

Fig. 2 shows the surface topography of natural textured titanium. Titanium samples were sputtered for 4 h at various angles of ion beam incidence varying from 0 to 1.4 rad. Images presented in Fig. 2 show the great influence of ion incidence on surface morphology of ion textured material. Different incidence angles "give" different images of sputtered surface. A lot of topographical features can be observed: (a) flat and shallow craters, and variously shaped hillocks on normally sputtered surface (Fig. 2a); (b) craters, slots, steps, "cone-like" features and isolated areas of grooves (etch lines) on surfaces irradiated on an average inclined beam (see Figs. 2b and c): and (c) etch lines or grooves, ridges and extensive topographical features similar to "scale-like" structure on surfaces bombarded by strongly inclined beam (Figs. 2d and e).

Topographical features observed on natural textured surfaces of titanium are also oriented along the ion beam direction. This is especially noticeable in the case of near-glancing ion beam incidence, i.e., for incidence angles of 1.22 and 1.4 rad.

Surface topographies of tantalum sputtered at various angles of ion beam incidence (from 0 to 1.4 rad) are presented in Fig. 3. The specimens were cut from polycrystalline 99% tantalum rolled sheet and natural textured for 2 h. All samples except those normally sputtered were ion beam irradiated along the direction of rolling. Figs. 3a to c show the surface morphology of three samples irradiated by perpendicular ion beam (Fig. 3a) and on an averagely inclined beam (Figs. 3b and c). The surfaces, smooth before ion bombardment, are modified with inclination towards texturing. All three surface topographies are pretty similar. Extensive grooves and ridges oriented along the direction of rolling as well as ion beam sputtering can be observed. Some microstructural features are also seen, i.e. shallow pits (Fig. 3a) and hummocks (Fig. 3b). It seems that ion sputtering can reveal surface structure induced by rolling of the tantalum sheet but this is distinctly visibly only for ion beam incidence angles from 0 to about 1.05 rad (0° to 60°), where the etch rate is sufficiently high to reveal this structure. The surface topography observed on tantalum samples sputtered by the strongly inclined ion beam is very similar to that observed on previous specimens, i.e. stainless steel and titanium specimens. This is a "scale-like" topography oriented along the tangential component of the ion beam.

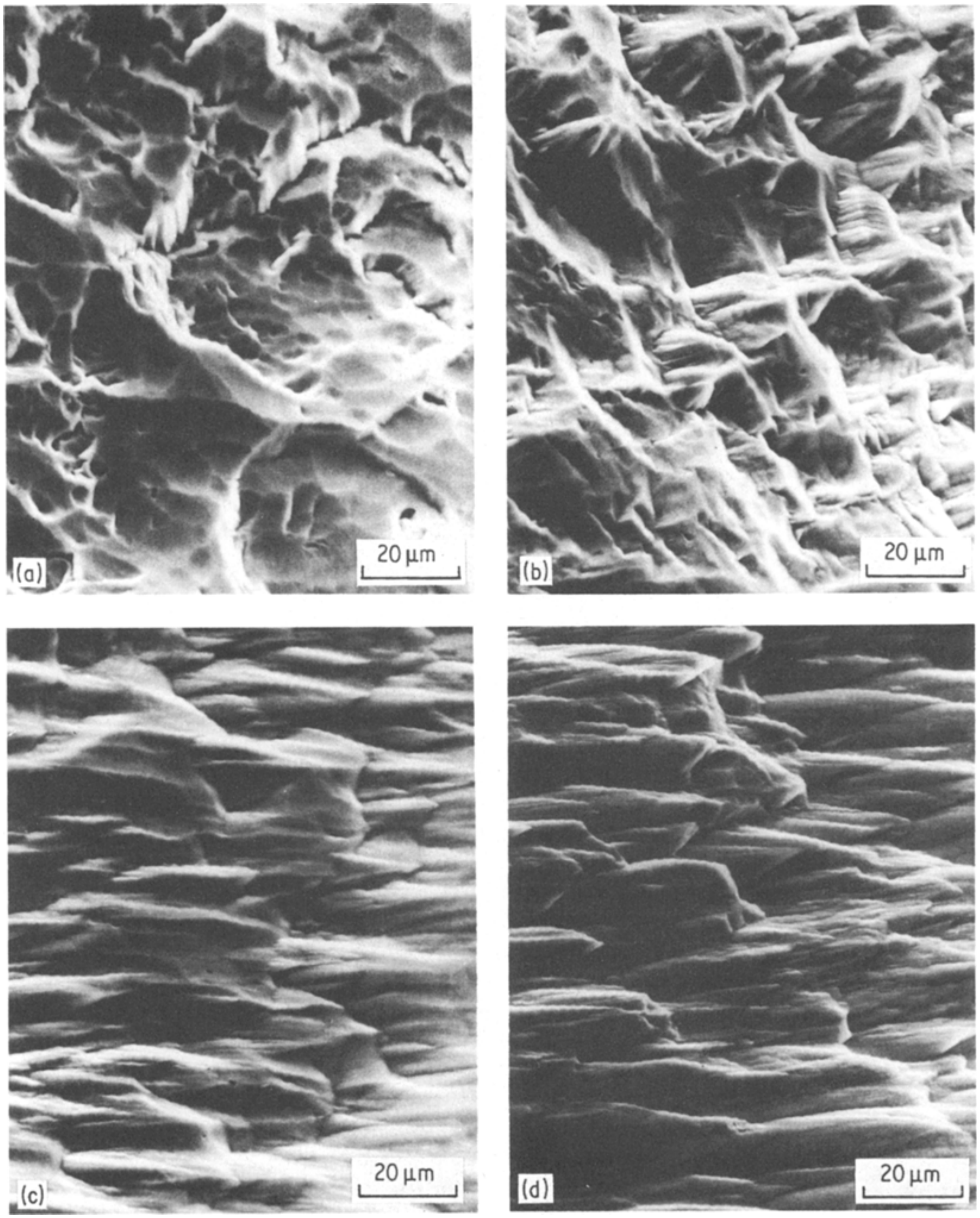


Figure 1 Scanning electron photomicrographs of natural textured chrome-nickel stainless steel, tilt about 0.8 rad. Samples were bombarded for 4 h at various angles of ion beam incidence. (a) Sample No. 1 at 0°; (b) sample No. 2 at 45° (~ 0.78 rad); (c) sample No. 3 at 60° (~ .105 rad): and (d) sample No. 4 at 70° (~ 1.22 rad).

The fourth material investigated was alumina. The samples of the material, in the form of plates 2 cm x 3 cm, were ion beam sputtered for 2 h at various incidence angles from 0 to 1.4 rad. SEM images of alumina surfaces before and after ion irradiation are shown in Fig. 4. The initial surface of the sample changes as a result of natural texturing. Grains and grain boundaries distinguished before ion beam bombardment are not visible after irradiation. It seems that the sputtering process can be considered as the erosion of the ion impact amorphized homogeneous and isotropic material containing pores and inclusions [16]. All images of ion sputtered alumina surfaces show the great

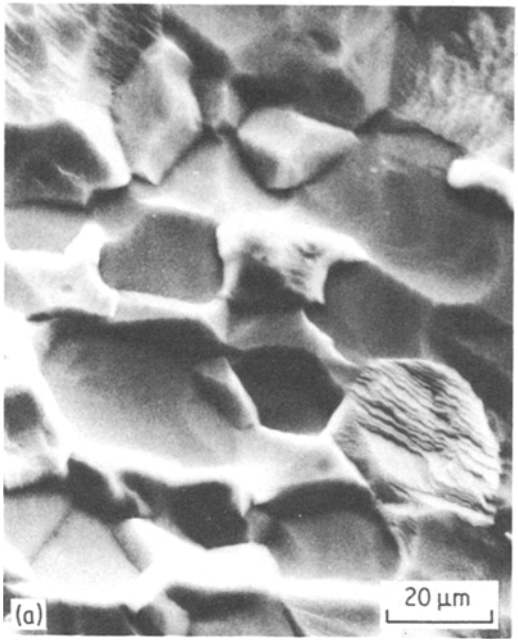


Figure 2 SEM images of titanium ion bombarded for 4 h at various incidence angles, tilt about 0.8 rad. (a) Sample No. 6 at 0°; (b) sample No. 7 at 45° (~ 0.78 rad): (c) sample No. 8 at 60° (~ 1.05 rad); (d) sample No. 9 at 70° (~ 1.22 rad); (e) sample No. 10 at 80° (~ 1.4 rad).

influence of the angle of ion beam incidence on surface topography. The topographical features observed are oriented along the tangential component of the ion beam. As formerly (see Figs. 1c, 1d, 2d, 2e, 3d, and 3e), surface topography of the specimens sputtered at very oblique incidence is very characteristic and resembles a "scale-like" structure.

In addition to the ion bombardment-induced changes in the surface topography, modification of surface roughness was also observed and measured. The roughness of the 99.5% alumina surface was calculated from the shape of the surface profile recorded by the profilograph. This profile is a rather distorted image for the actual surface topography due to the size of the diamond tip relative to the dimensions of the topographical features to be detected on one hand and to the enormous difference in scale between horizontal and vertical direction on the other hand [17]. The calculation method is presented elsewhere [18]. Introducing a coefficient $K = R_A/R_B$, where R_A is the mean roughness after ion irradiation and R_B is the mean roughness before ion bombardment, shows the changes of the roughness. The angular dependence of the maximum, minimum and mean coefficients for Ar^+ irradiation of 99.5% alumina surface is described in Table III. Table IV shows the angular dependence of the mean coefficient K_m for argon ion bombardment of some alumina samples selected from the specimens described in Table III. SEM images of surfaces of these selected samples are presented in Fig. 4. A substantial increase of surface roughness ($K > 1$) is seen for perpendicular bombardment. For very oblique ion incidence roughness is greatly reduced.

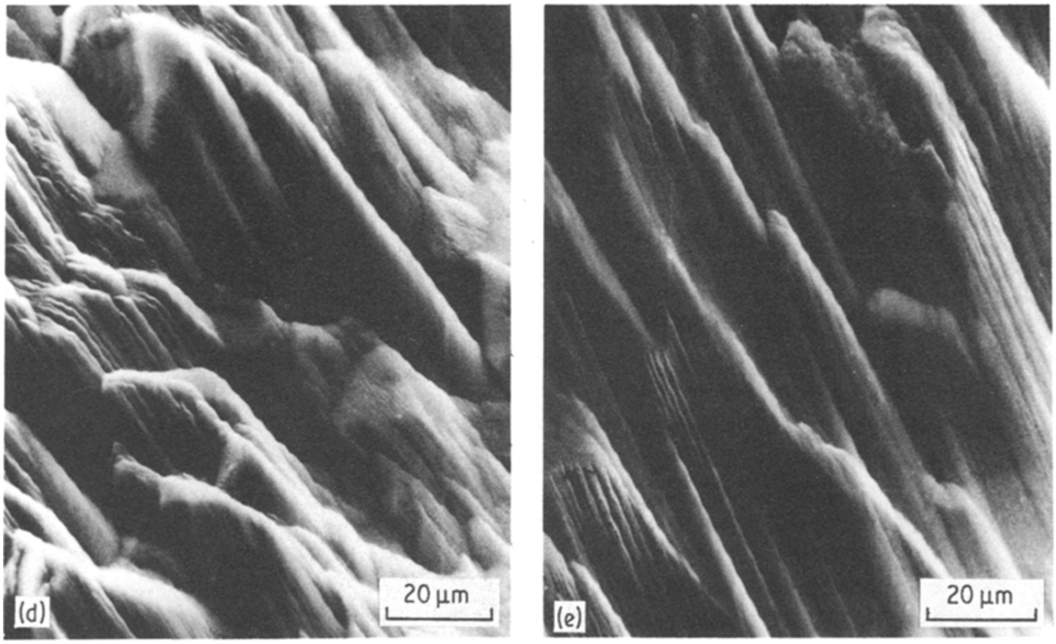


Figure 2 Continued.

The experimental results presented in this paper show that ion sputtering at various angles of ion incidence can modify surface topography and roughness of biocompatible materials in a controlled manner. A great many topographical features are developed and can be observed on ion irradiated surfaces of biomatierals and/or biocompatible materials but at very oblique incidence one characteristic topography or structure is seen. This is a "scale-like" topography with different sized and shaped scales and etch lines oriented along the tangential component of ion beam.

4. Discussion

Theoretical problems relating surface morphology changes have been studied for many years [19–25].

Experimental observations of ion sputtered surfaces of solids reveal the influence of ion sputtering conditions, particularly the angles of incidence, on the morphology of the ion-bombarded surface, which exhibits etch lines and "scale-like" or "scale-shaped" topography (or structure [26]) and other topographical features presented in Table V. In most cases, the sputtered topographical features are oriented along the tangential component of the ion beam.

It is difficult to say anything definite about the mechanisms of formation of these features but two points should be stated:

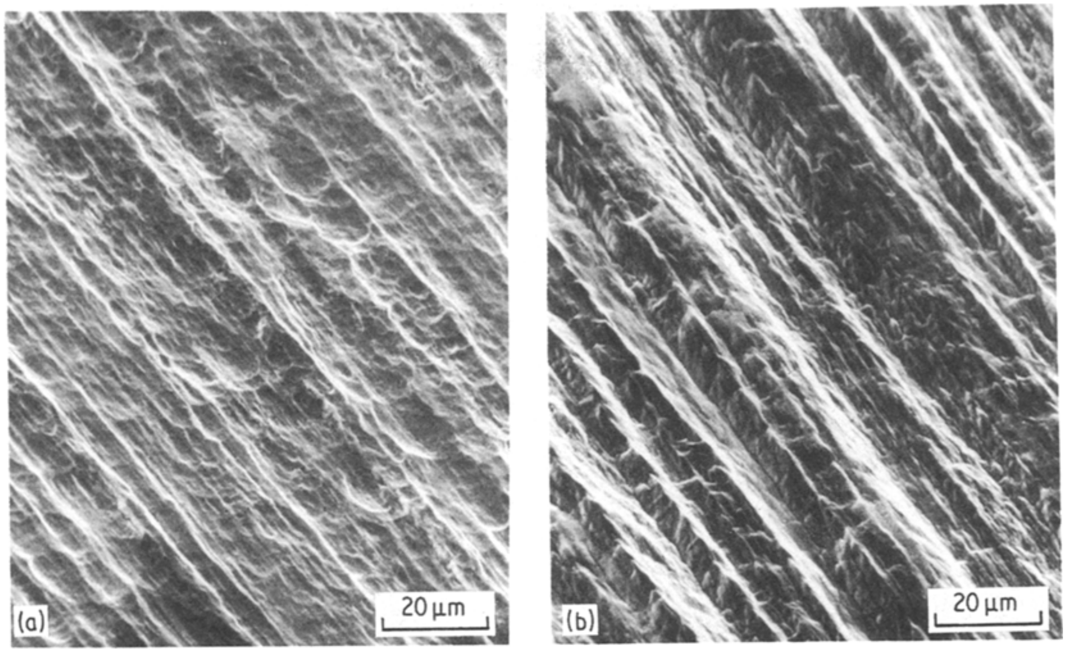
(a) It seems that observed topographical features such as etch lines, "scale-like" or "scale-shaped" topography are rather general.

TABLE III Angular dependence of the K_{max}, K_{min}, and K_m coefficients for Ar^+ irradiation of 99.5% alumina surface (accelerating voltage of about 7 kV, ion beam density up to 0.5 mA cm^{-2}, ion source–sample distance of 1.5 cm, duration about 2 h)

Beam incidence angle, θ (rad)	Maximum coefficient, K_{max}	Minimum coefficient, K_{min}	Mean coefficient, K_m
0	2.12	0.97	1.29
~ 0.78 (45°)	0.78	0.74	0.76
~ 1.05 (60°)	1.08	0.69	0.88
~ 1.22 (70°)	0.94	0.66	0.79
~ 1.4 (80°)	0.71	0.59	0.65

TABLE IV Angular dependence of the mean coefficient K_m for Ar^+ bombardment of some alumina samples selected from Table III studied by SEM – see Fig. 4

Beam incidence angle, θ (rad)	Mean coefficient, K_m	Sample number	Fig. number
0	1.17	16	4b
~ 0.78 (45°)	0.76	17	4c
~ 1.05 (60°)	0.69	18	4d
~ 1.22 (70°)	0.68	19	4e
~ 1.4 (80°)	0.60	20	4f



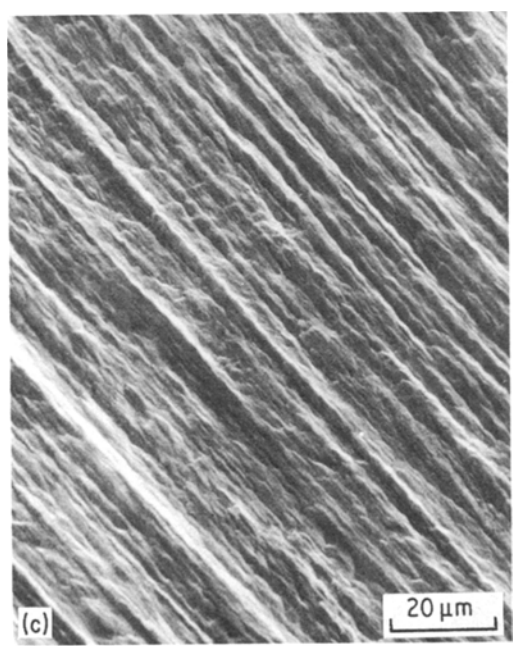


Figure 3 Surface topography of tantalum after ion sputtering at various angles of ion beam incidence, tilt about 0.8 rad. (a) Sample No. 11 at 0°; (b) sample No. 12 at 45° (~ 0.78 rad); (c) sample No. 13 at 60° (~ 1.05 rad); (d) sample No. 14 at 70° (~ 1.22 rad); (e) sample No. 15 at 80° (~ 1.4 rad).

(b) The angle of ion incidence is the main parameter which influences the development of topographical features mentioned above.

The great influence of the angle of ion beam incidence on the surface morphology is distinctly visible in the case of biomaterials (and/or biocompatible materials). Topographical features observed on the surfaces of stainless steel, titanium, alumina and tantalum samples are in fact oriented along the tangential component of the ion beam. Surfaces of all the samples studied sputtered at very oblique angles of ion beam incidence have a "scale-shaped" topography with numerous lines, channels, grooves, etc., etched along the ion

TABLE V Some topographical features observed at the ion irradiated surface of solids

Feature name	Kind of material sputtered	References
Cone	Metals, semiconductors, alloys, glass, resin	[11, 27–34]
Hummock, Hillock	Glass, metals	[29–31, 35–38]
Pit, Crater	Metals, semiconductors, glass	[27, 30, 31, 33–36, 39]
Groove, Furrow	Metals	[24, 29, 31, 36, 37, 40]
Ridge	Metals	[11, 31, 32]
Step	Metals, semiconductors	[30, 32, 36]

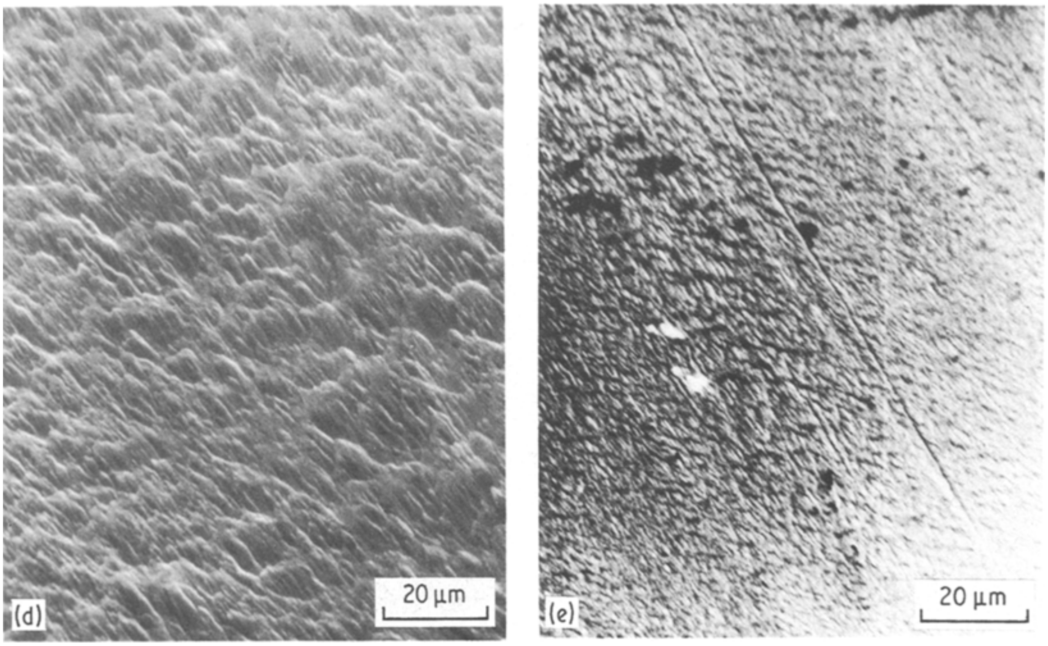


Figure 3 Continued.

beam direction. For these ion incidence angles ion sputtering is dominated by collisions occurring in the top surface layers. The mechanism of formation of topographical features mentioned above is a phenomenon located near the surface, but it is more complicated because these first layers of polycrystalline samples of biocompatible materials studied are amorphized during ion beam irradiation. Teodorescu and Vasiliu [26] have stated that to explain the etch lines and "scale-shaped"

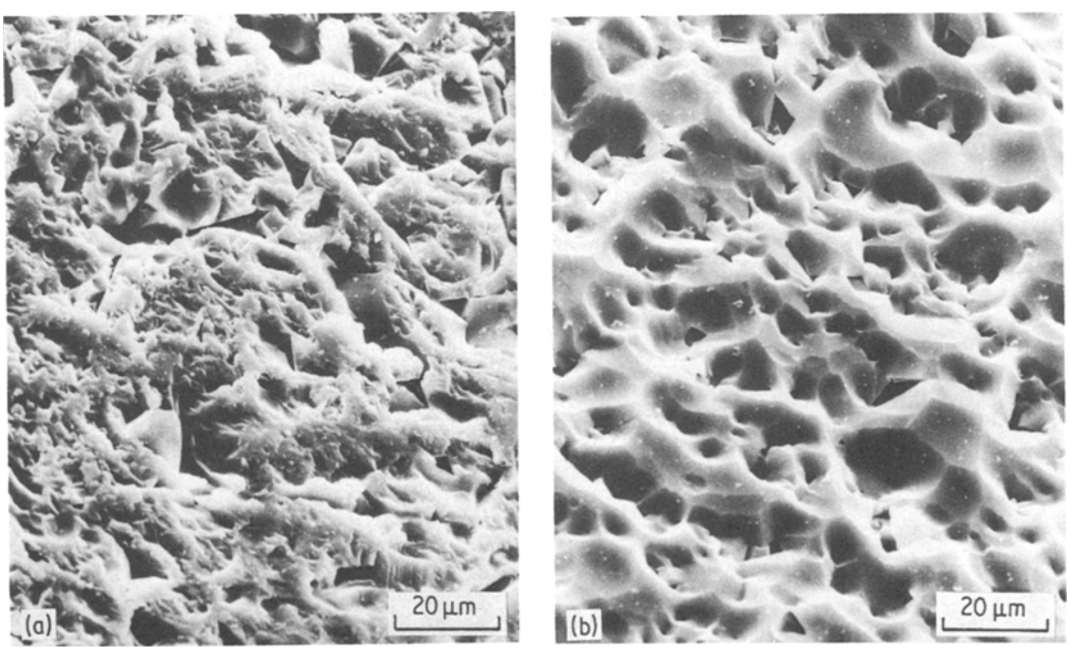


Figure 4 Surface topography and mean roughness of alumina after ion beam irradiation at various beam incidence angles, tilt about 0.8 rad. (a) Untreated surface; (b) sample No. 16 sputtered at 0°, $K_m = 1.17$; (c) sample No. 17 bombarded at 45° (~ 0.78 rad), $K_m = 0.76$; (d) sample No. 18 irradiated at 60° (~ 1.05 rad), $K_m = 0.69$; (e) sample No. 19 after sputtering at 70° (~ 1.22 rad), $K_m = 0.68$; (f) sample No. 20 after ion irradiation at 80° (~ 1.4 rad), $K_m = 0.60$.

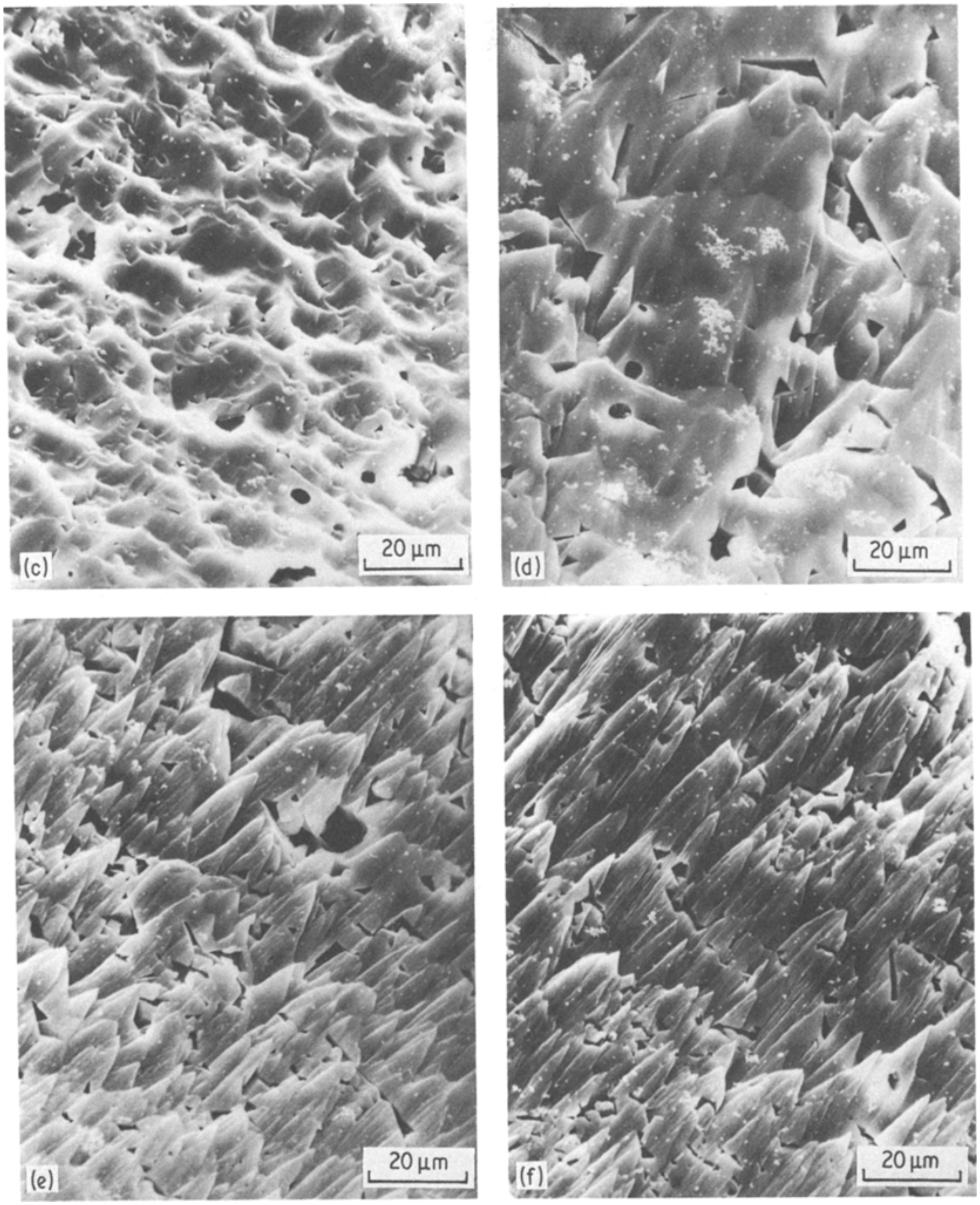


Figure 4 Continued.

topography produced by ion bombardment one sould use the mechanism which takes into consideration the following: (a) the initial geometry of the sample surface; (b) the strong dependence of sputtering yield on ion incidence angle.

In our experiments the initial geometry of the sample is unimportant. For very oblique ion beam incidence the etch lines and "scale-shaped" topography can be seen not only on initially rough surfaces (titanium and alumina) but also on smooth surfaces (stainless steel and tantalum). It seems that the main reason on formation of such topographies is the great influence of ion beam incidence angle on the sputtering yield.

5. Conclusions

Ion beam sputtering has proved to be a valuable tool in the preparation of surfaces of biomaterials and/or biocompatible materials. This technique can modify the surface topography and roughness of the materials in question. The feasibility of this method was confirmed by SEM and profilograph examinations. Experimental results have shown that the angle of ion beam incidence is a very important parameter, which influences both the surface topography and roughness. Using the first ion texturing technique, i.e. natural texturing and various angles of ion beam incidence, it is possible to change the surface morphology of biomaterials in a controlled manner and avoid contamination problems, which is a very important fault of the other two techniques of ion beam texturing (i.e. seed texturing and pattern texturing). The resulting surface morphology may potentially be used to improve the biological response to implant materials and to modify the mechanical properties of these materials.

Acknowledgements

The author is indebted to Dr S. Smardz and Mr J. Szymański for their help in the experimental work.

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Received 18 July and accepted 1 November 1983