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Conical Surface Textures Formed by Ion Bombarding 2% Be Cu Alloy*

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A homogeneous, micrometer-sized conical surface texture forms on 2% Be-Cu alloy which is bombarded with an argon beam produced by a Kaufman ion source. The dimensions of the features that form strongly depend on: 1) argon energy (from 250 to 1500 eV), 2) fluence (10^{19} to 10^{20} ions/cm^2), and 3) flux (0.1 to 1 mA/cm^2). The texture morphology depends less strongly on the background ambient (Mo vs. graphite), earlier alloy heat treatments and the temperature during bombardment (100°C and 450°C). As the texture matures with increasing fluence, the number of large features increases at the expense of the number of small features. The observed relationship between texture formation and ion flux suggests that the evolution of these features is not adequately described by theories predicting that the mature conical sidewall angle is related to the angle of the maximum sputtering yield. These textured surfaces can be coated with other metals for a variety of possible applications including: 1) pulsed power Li+ beam anodes, 2) cold cathode field emission devices, 3) optical absorbers and 4) catalysis supports.

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I. Introduction

Observations of the formation of micrometer-sized features on ion bombarded surfaces of certain metals have an extensive history. In the 1930's, when sputtering was first popularly employed as a coating deposition technique, researchers observed that some sputtering targets developed a matte appearance after continued use; a corresponding decrease in sputter yield typically occurred.[1,2]

In the 1950's, Wehner began a series of careful, systematic, fundamental studies of the development of cone or whisker-like features on ion bombarded materials that was to continue for more than three decades.[3-6] Wehner and his collaborators, and other reseachers[7-11] searched for materials and conditions that gave rise to cone or whisker formation. These investigators observed that cone formation frequently occurs when a metal is ion bombarded in the presence of a "seed" - a trace amount of an element with a higher sputtering yield or a higher melting temperature. Qualitative studies indicated that conical features form on certain alloys such as stainless steel and 2% beryllium-copper.[5] Many groups have intensively studied the formation of conical features on high purity copper that is ion bombarded in the presence of trace amounts of a variety of seed materials including molybdenum or carbon.[3,4,10,12-14]

In the late 1970's, interest in conical surface features on ion bombarded surfaces expanded from a fundamental basis to an applied basis with an increased interest in magnetically confined fusion reactors as commercially viable energy sources, and the recognition of the "first wall problem". Texturing the "first wall" surfaces of reactor materials exposed to the plasma was proposed as a technique for reducing the amount of relatively high atomic number atoms sputtered into the hydrogen plasma that would cool the plasma.[15] Homogenoous, micrometer-sized, conical surface topographies may also find applications as: 1) pulsed power ion beam anodes, 2) cold cathode field emission devices, 3) optical absorbers, and 4) catalysis supports. For these applications, the abilty to form homogeneous features over a relatively large area is a prerequisite. Much of the attention of the earlier studies was directed towards observing the formation of a relatively few inhomogeneously sized cones in relatively small discontinuous areas over the surface of the bombarded material.

Here we briefly report results from our preliminary screening studies with: 1) stainless steel, 2) high purity copper, and 3) 2% beryllium-copper that were placed on either: 1) molybdenum or 2) graphite backing sheets and bombarded with argon. During these preliminary studies, our goal was to learn if it is possible to form homogeneous features over a large area. Of these three candidate materials, the material that responded best was 2% beryllium-copper. The relationships that we observed between the bombardment conditions and the development of features on 2% beryllium-copper samples are reported here in greater detail.

II. Experimental

Samples of 304 annealled stainless steel, oxygen free high conductivity copper and 2 wt% beryllium-copper with surface areas from 1 to 4 cm^2 and an initial surface finish of 0.7 micrometers root-mean-square or smoother were ultrasonically cleaned in detergent and water, then rinsed with water and dried in lab air. Some beryllium-copper samples were used in the as-received temper. Other beryllium-copper samples were heat-treated in vacuum at 700°C for 30 min, or 850°C for 180 min. The copper and the beryllium-copper samples were etched for 2 min in a 50 volume% HNO_3 solution, rinsed with water, then rinsed with absolute ethanol and dried shortly before use. (This procedure produces a Be-rich surface on the beryllium-copper samples.) After being etched with HNO_3, some samples of beryllium-copper were etched for extended periods of time, 60 min, in hot, 90°C, saturated NaOH, then rinsed with water and with ethanol. (This procedure produces a Cu rich surface.)

The clean samples were placed on 8 cm diameter, 99.9 % pure molybdenum or graphite sheets for the preliminary study, or on a graphite sheet for the detailed study. In the preliminary study, the samples were partially masked with small pieces of molybdenum or graphite; the sputtered molybdenum or carbon ambient was highest close to the perimeter of the mask. By doing this, we hoped to observe any strong dependency between cone formation and the ratio of the impurity atom flux to the bombarding ion flux. Some samples were placed on a small, molybdenum- or a graphite-clad resistive heater on top of the larger sheet during the preliminary screening study. The sheet with many small samples was in turn placed upon a 7.5 cm diameter water cooled target platform of a Veeco Microetch system that employs a Kaufman ion source producing a 7.5 cm diameter ion beam. The ion beam system was pumped using a 25 cm diameter expanded diffusion pump yielding a background pressure of 10^{-6} T. Ultrahigh purity argon was used as a working gas at a pressure of approximately 10^{-4} T (in the target chamber). The samples were bombarded with argon at maximum ion energies from 250 to 1500 eV, at fluxes from 0.1 to 1.5 mA/cm^2, for periods extending from 30 min to 6 hr, which corresponds to a fluence of 10^{19} to 12×10^{19} ions/cm^2 at 1 mA/cm^2. The samples on the water cooled platform rose to temperatures no higher than 100°C; the heated samples were typically maintained at 450°C. After bombardment, the samples were examined visually for regions with a matte, velvet, or darkened appearance that indicated a considerable area with an ion bombardment evolved conical or columnar surface texture. Representative samples were examined at low and high magnification using a scanning electron microscope (SEM). Energy dispersive x-ray analysis (EDX) and electron microprobe analysis were used to try to identify the elements present on representative sample surfaces.

In order to determine whether a deposited coating would replicate the surface texture and provide an alternative surface chemistry, certain texturized beryllium-copper samples were coated with 50 to 500 nm of chromium using an electron beam evaporation system that was equipped with a rapidly rotating planetary substrate mount.

III. Results and Discussion

Cones were observed on the surfaces of all three metals after ion bombardment with 1500 eV argon ions at 1 mA/cm^2 for six hours at sample temperatures of less than 100°C, and 450°C. Similar results were observed with the graphite and the molybdenum backing sheets. The cones that formed on the copper (Figure 1) and the stainless steel surfaces (Figure 2) appear at isolated areas relatively close to the edges of the molybdenum or graphite masks placed on these substrates. The cones that form on copper (Figures 1a, 1b and 1c) and stainless steel (Figure 2b) vary in size. On the copper surfaces, the cones are scattered both singly and in clusters. The cones forming on the stainless steel surfaces follow a pattern that suggests that they may be, to some extent, associated grain boundary sites (compare Figure 2a to Figure 2b). On other areas of the ion bombarded copper and stainless steel surfaces, coral-like structures (Figure 1b) and mesa-like features (Figures 2c and 2d) form. No cones, coral-like features or mesas were seen on bombarded areas that were far from the perimeters of the masks on the copper and the stainless steel samples. These more remote areas were roughened with grain decoration; (compare Figures 2e and 2f to Figure 2a, the as-received surface of the stainless steel).

The distribution of the cones over the ion bombarded copper and stainless steel samples is very different from the distribution of the cones over the ion bombarded beryllium-copper samples (Figure 3). A relatively homogeneous distribution of cones formed uniformly over the entire ion bombarded beryllium-copper surface, independent of distance from the perimeter of any mask. This homogeneity and uniformity may indicate that far less carbon or molybdenum is required to seed cone formation on beryllium-copper as compared to stainless steel or copper, or that there is a relatively homogenous supply of seed material intrinsically in this alloy; alternatively, some other entirely different mechanism may be initiating cone formation here. Beryllium may be seeding cone formation from the copper in this alloy. The melting temperature of beryllium at 1 atm., 1278°C, is higher than the melting temperature of copper, 1083°C; the reseachers who have postulated that high melting temperature metals seed cone formation on lower melting temperature metals would predict that beryllium could seed cone formation on copper. The sputter yield of beryllium is (depending on argon ion energy) from 25% to 50% that of copper[16]; the reseachers who have postulated that low sputter yield metals seed cone formation on metals that sputter more readily would predict that beryllium could seed cone formation on copper.

Because a homogeneous network of cones can be formed over large areas of beryllium-copper, this technique may be useful for tailoring surface topographies for a variety of applications, such as pulsed power lithium ion beam anodes. For this reason, we characterized the conditions that affect cone formation to greater detail for beryllium-copper than for copper or stainless steel. The formation of cones on beryllium-copper alloy was not observed to be affected by prior heat-treatments: 1) as-received stock vs. material heated in vacuum to 2) 700°C for 30 min, and 3) 850°C for 3 hr. Samples with a beryllium rich surface (HNO_3 etch) responded similarly to samples with a copper rich surface (hot NaOH etch). Samples at 450°C developed features at approximately the same rate as samples at ambient temperature.

The microstructure of the cones that formed on samples placed on a graphite backing sheet appeared in SEM views to be very similar to the microstructure of cones from samples on a molybdenum backing sheet. Visually the samples were different. The texturized samples from the graphite runs had a velvet reddish brown appearance. Samples from the molybdenum runs were typically velvet black. This variation in color is probably related to a small variation in the average size or spacing of the features, which is not apparent in the small fields of view shown in the high magnification SEM micrographs. No significant amounts of backing plate elements or other elements were detected on any of the bombarded surfaces using energy dispersive x-ray analysis; (the extremely rough surface topographies here compromise the sensitivity of the surface elemental analysis techniques used).

The size of the cones formed on beryllium-copper depend on: 1) ion fluence, 2) ion beam energy, and 3) ion flux. Figure 3 shows the surface of samples after bombardment with 1500 eV argon, at a flux of 1 mA/cm^2, at fluences of: a) $2x10^{19}$ $ions/cm^2$ and b) $7x10^{19}$ $ions/cm^2$. Relatively small features form first. With continued bombardment, these features ripen into large mature features. With an ion flux in the range of 0.5 to 1.5 mA/cm^2, at a given fluence, smaller features are observed with lower ion energies; no bombardment runs longer than 6 hr were performed to determine whether these small, low energy cones would eventually mature into large cones. A certain minimum ion flux is required to form and maintain the cones. Cones formed at a flux of 0.5 mA/cm^2 or above (Figure 4a) are "erased" if they are bombarded with ions at extremely low current densities, i.e., 0.1 mA/cm^2 or less (Figure 4b). This observation indicates that the currently accepted model used to describe cone growth and steady state maintenance on an ion bombarded surface requires, at least, subtle revision. It has been proposed that the sidewall angle of stable mature cones on an ion bombarded surface is related to the angle of the maximum ion erosion yield.[17] From Lindhard's[18] first principle theory, the angle of the maximum ion erosion yield θ (in radians) is a function of ion energy E (eV), the atomic numbers of the bombarding ion and the material bombarded Z_1 and Z_2, and the (average) distance between the atoms in the material being bombarded d (Ångstroms),

$$\theta = \left(\frac{3ae^2 Z_1 Z_2}{4\pi\varepsilon_0 E d^3}\right)^{1/4}$$

where e is the charge of an electron (14.4 eV Å), $1/(4\pi\epsilon_0) = 1$, and a is the Thomas-Fermi screening radius,

$$a = \frac{0.8853a_o}{\left(Z_1^{2/3} + Z_2^{2/3}\right)^{1/2}}$$

Here a_o is the Bohr radius (0.53 Å). The angle of the maximum ion erosion yield described by this generally accepted theory does not depend directly on flux; the ability to maintain stable cones on an ion bombarded beryllium-copper surface requires a bombarding flux that is above a certain minimum value that our observations indicate is within the range of 0.1 to 0.5 mA/cm^2. It is probable that higher ion current densities give rise to higher near-surface temperatures and greater metal atom mobility in the near-surface region. Our observation that some minimum ion fluence is necessary to maintain stable cones may indicate that, in addition to ion erosion, surface transport somehow plays a role in the evolution these surface topographies.

For certain applications, a conical surface topography chemistry other than beryllium-copper may be preferable from the standpoint of wetability or reactivity considerations. Representative samples of texturized beryllium copper were coated with a nominal thickness of chromium from 50 to 500 nm using an electron beam deposition system with a rapidly rotating planetary substrate mount (to improve coating conformity). The surfaces and the profiles of the coated samples were then examined using the SEM; EDX and an electron microprobe were used to analyze the elemental chemistry of the near-surface region. The microstructure of the coated samples all appeared to be similar to the uncoated samples (Figures 5a and 5b). (Visually the uncoated samples were a velvet reddish brown; the coated samples were velvet black.) All of the nominal chromium thicknesses appear to replicate the underlying topography of the texturized beryllium-copper. Energy dispersive x-ray analysis detected Cr at both the tops and the bases of cones on profiled samples; EDX does not have sufficient resolution, however, to determine how uniform these Cr coatings are, or whether these coatings are free of pinholes.

The electron microprobe also indicated Cr spread over a band corresponding approximately to the height of the cones (Figure 5c). Resolution limitations do not allow a more quantitative evaluation of these coated samples with the microprobe. Our results indicate that a coating can be applied to a texturized surface to alter its wettability. Our data are insufficient to determine whether the coatings are uniform and can be used to protect the beryllium-copper from chemical attack.

IV. Summary and Conclusions

We have bombarded samples of 304 stainless steel, copper and 2% beryllium-copper alloy with argon ions in an ambient of carbon and molybdenum seeds and attempted to form micrometer-sized cones. Patches of cones of varying sizes formed on the stainless steel and the copper samples in areas that were relatively close to sources of sputtered carbon and molybdenum seeds. A uniform homogeneous distribution of cones formed over the entire bombarded surface of the beryllium-copper samples. Smaller cones formed on the beryllium-copper at lower fluences (10^{19} to 10^{20} Ar/cm^2) and at lower argon energies (250 to 1500 eV). An ion flux in excess of a minimum value in the range of 0.1 to 0.5 mA/cm^2 is required to maintain mature cones on a surface exposed to continued ion bombardment. This result suggests that, in addition to ion erosion, surface and/or near surface transport is important with regards to cone formation. Conformal chromium coatings can be deposited on these topographies on beryllium-copper to alter their surface chemistry.

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FIGURE CAPTIONS

FIGURE 1. Surface features found on the surface of copper after bombardment with 1500 eV argon at a current density of 1 mA/cm^2 for six hours with molybdenum seeds. a) Relatively low magnification view showing the distribution of cones in an area that was relatively close to a source of Mo. b) A coral-like topography observed on a different area of the same sample. c) and d) Two larger magnification views showing the variation in cone size at different areas on the same sample. Similar results were observed when a graphite sheet was used to supply seed material.

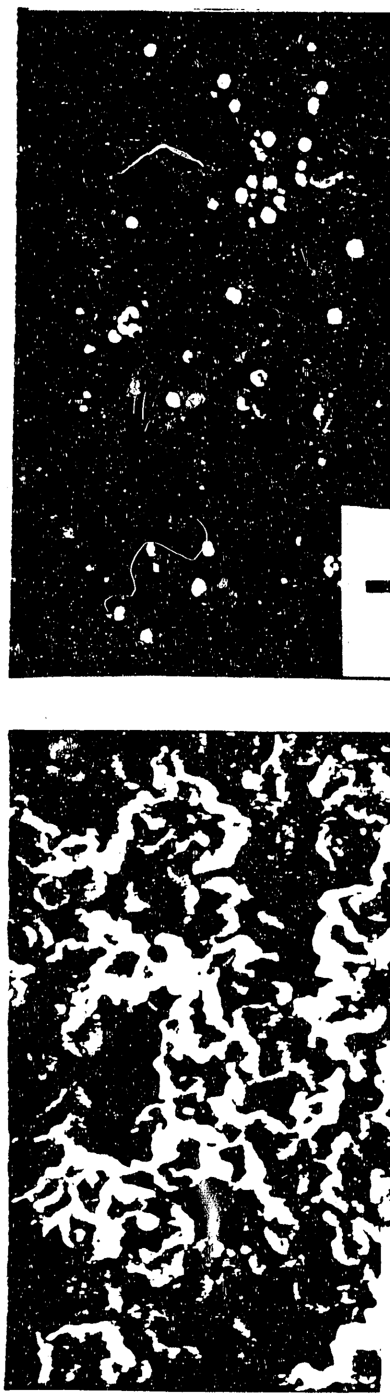
FIGURE 2. Surface features found on the surface of stainless steel after bomdardment with 1500 eV argon at a current density of 1 mA/cm^2 for six hours with molybdenum seeds. a) The surface of the sample before bombardment. b) Relatively low magnification view showing the distribution of cones in an area that was relatively close to a source of Mo. c) and d) A mesa-like topography observed on a different area of the same sample. e) and f) Grain decoration on other areas of the same sample. Similar results were observed when a graphite sheet was used to supply seed material.

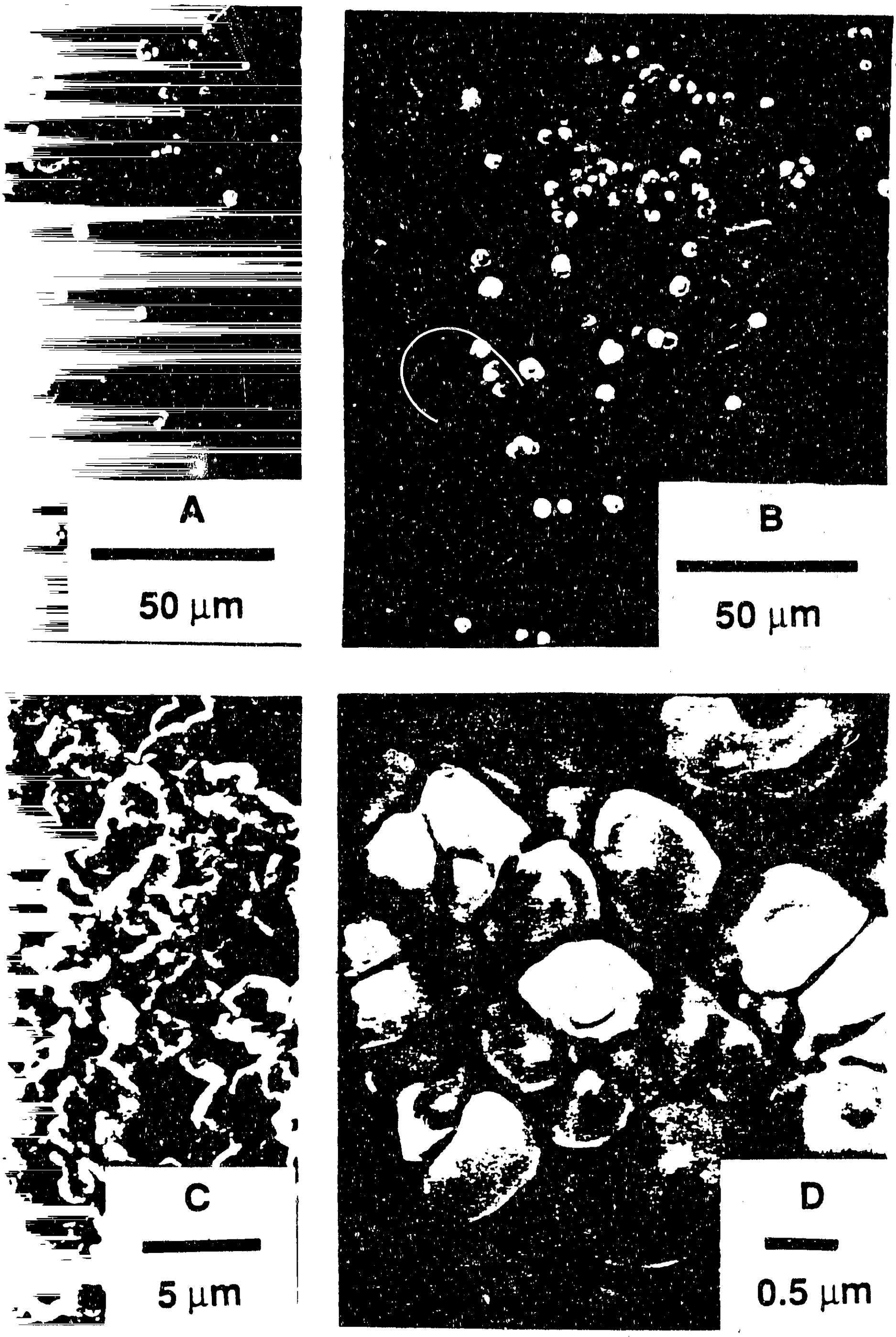
FIGURE 3. Cones formed on 2% beryllium-copper bombarded with 1500 eV argon, 1 mA/cm^2, ambient temperature, carbon ambient. a) after 10^{10} $ions/cm^2$ (1 hr.), b) after $7x10^{19}$ $ions/cm^2$ (3 hr.). As fluence increases, the size of the cones increases.

FIGURE 4. Textured surfaces formed by bombarding 2% beryllium-copper with 500 eV argon, carbon ambient. a) after 60 min. bombardment at 0.6 mA/cm^2. b) the same sample after an additional eposure at 0.1 mA/cm^2 for 60 min. An exposure at low current density erases

the texture formed during previous exposure at a higher current density.

FIGURE 5. A texturized 2% beryllium-copper sample (500 eV argon, 0.7 mA/cm^2, 3 hr.) which has been coated with a nominal thickness of 500 nm Cr. a) Overview, b) cross-section. c) an electron microprobe map of Cr over a similar area at the same magnification shown in view b). (For the gain factor used, in regions with a Cr concentration of 20 at.%, the film would be totally exposed). The chromium coating replicates the underlying surface topography.




A
50 µm
B
50 µm
C
5 µm
D
0.5 µm

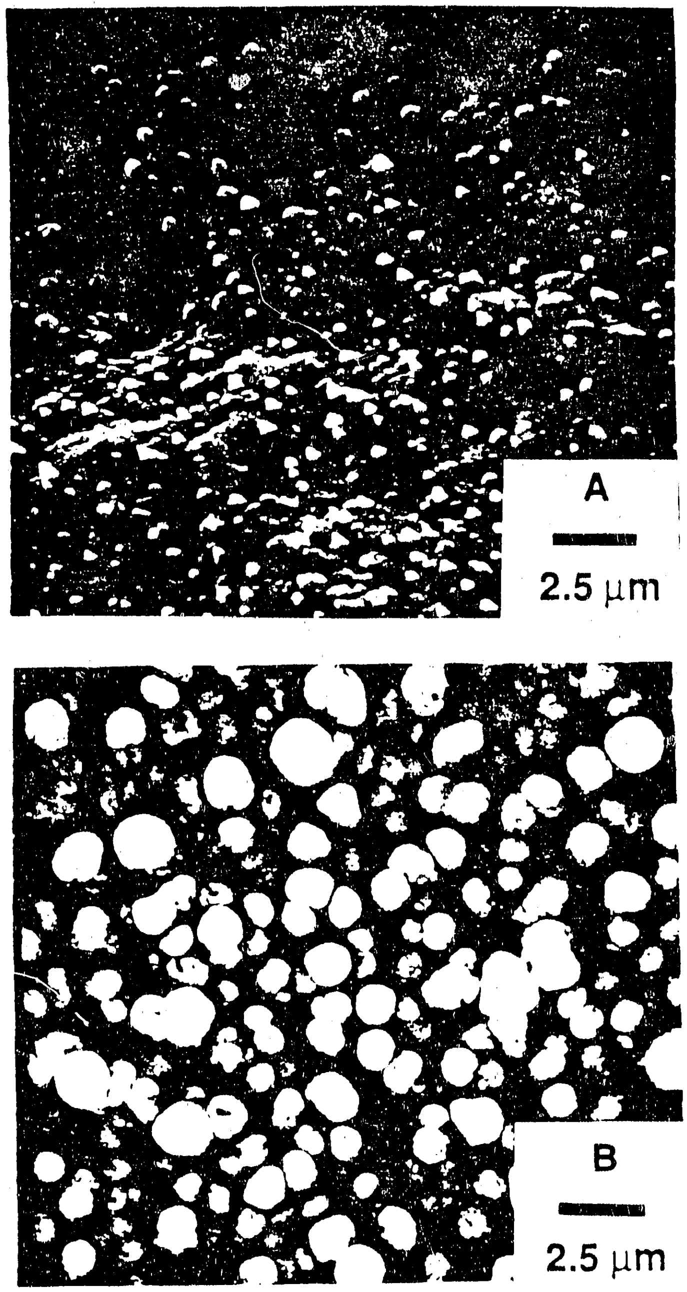


FIGURE 3

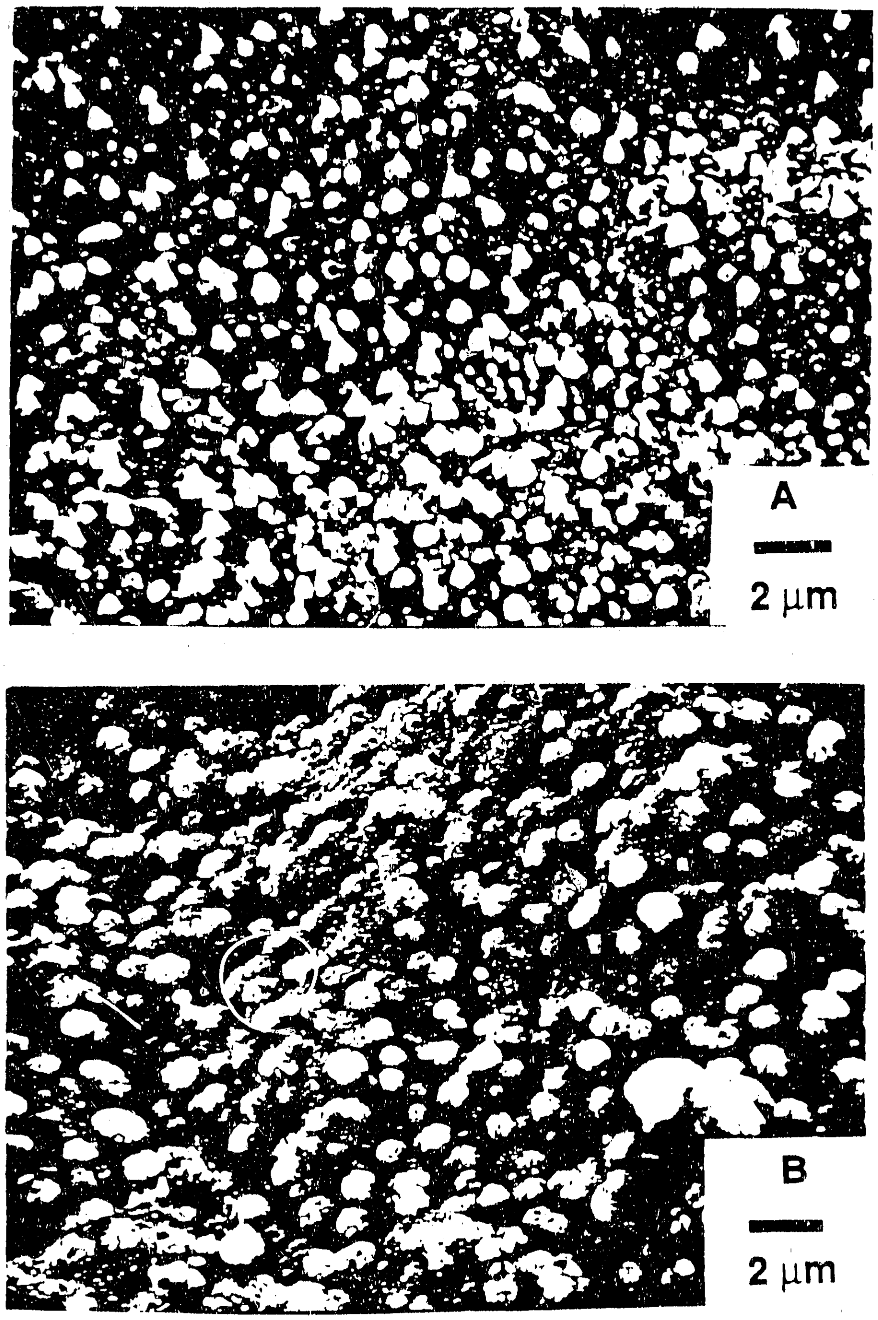


FIG. 4

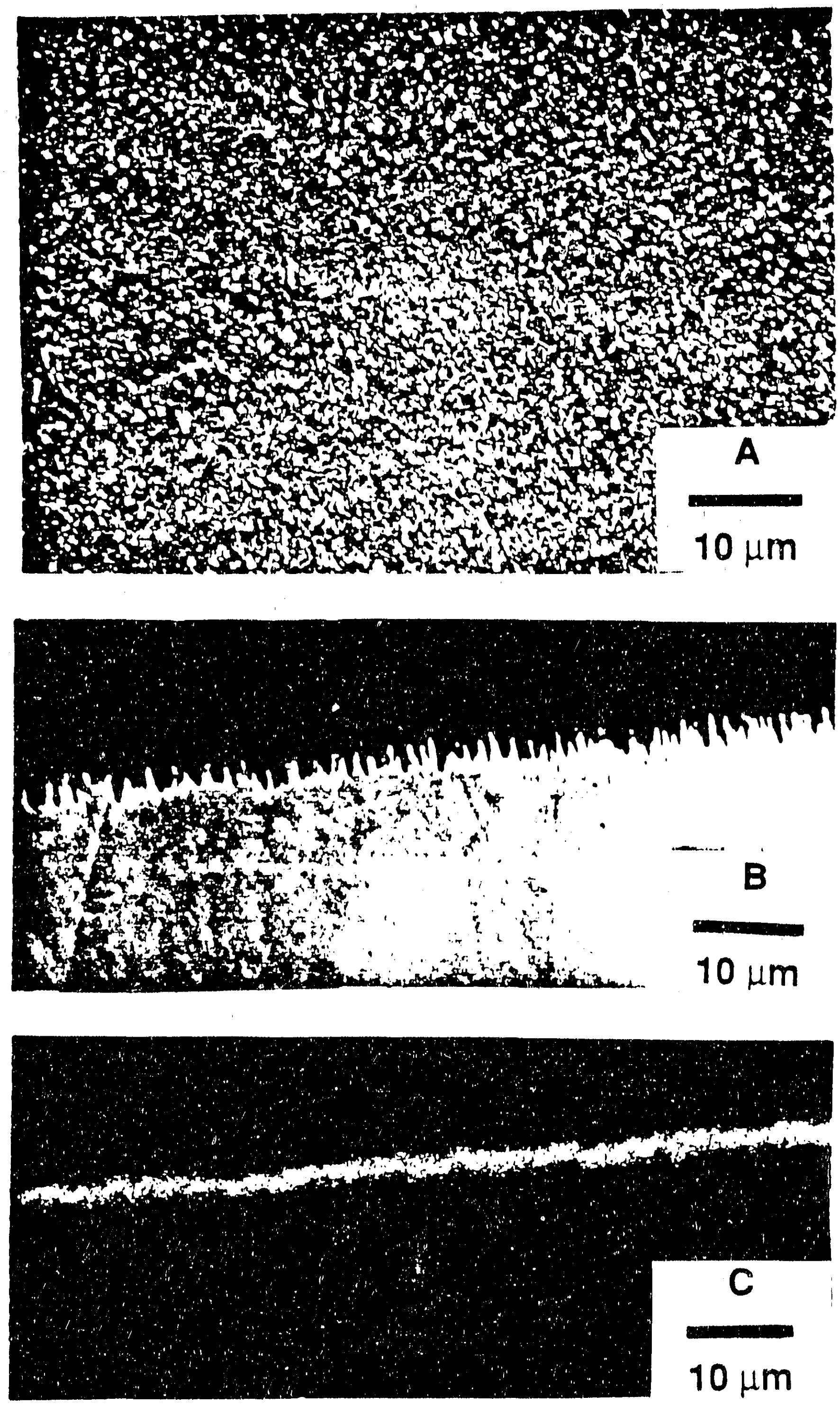


FIG. 5

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