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Diamond Growth on Carbide Surfaces Using a
Selective Etching Technique

by

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Diamond Growth on Carbide Surfaces Using a
Selective Etching Technique

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Microwave plasma-enhanced chemical vapor deposition of diamond films on silicon carbide and tungsten carbide (with 6% cobalt) surfaces using fluorocarbon gases has been demonstrated. No diamond powder pre-treatment is necessary to grow these films with a (100) texture. The diamond films are characterized by scanning electron microscopy and Raman spectroscopy. The proposed nucleation and growth mechanism involves concurrent etching of the non-carbon component by atomic fluorine and deposition of diamond. Hydrogen is necessary in the growth process to limit the rapid etching of the substrate by fluorine atoms.

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INTRODUCTION

Diamond has an impressive array of physical and mechanical properties that make it an attractive material in a variety of industrial applications. With the advent of chemical vapor deposition (CVD) techniques, thin film diamond can be deposited on a variety of substrates; however, problems remain to be solved. A major impediment to wide-scale utilization of these films is the need to abrade/seed the substrate with diamond in order to have sufficient nucleation density.¹ The seeding step produces scratches and leaves sub-micron diamond seeds on the substrate surface to serve as nucleation sites. Alternative means have been developed to circumvent this seeding step. These include carbon ion implantation into the substrate²⁻⁵, the use of an ion beam to create crater arrays on the surface⁶, coating the substrate with fullerenes⁷⁻⁸, utilizing various buffer layers⁹⁻¹², bias-enhanced nucleation¹³⁻¹⁵, or the use of graphite as a substrate.¹⁶ Meilunas et. al.⁷⁻⁸ thermally sublimated C₇₀ onto silicon substrates and activated the C₇₀ in a plasma environment by biasing of the substrate. Nucleation densities comparable to diamond grit polished silicon (10¹⁰ / cm²) were found. Hydrogenated amorphous carbon interlayers are found to produce a nucleation density approaching 10⁷ /cm² on silicon with lower densities found on other substrates¹⁰. A recently reported technique¹³⁻¹⁵ involves a three step process consisting of pre-treatment, bias nucleation, and growth. The pre-treatment step forms a thin silicon carbide (SiC)

layer on the surface. Biasing the substrate enhances the nucleation density of the diamond and produces a large percentage of diamond grains oriented with respect to the underlying silicon. Growth proceeds with fairly conventional diamond CVD process parameters. Most of these investigations listed above rely upon the deposition or placement of non-diamond carbon on the substrate to start the nucleation process.

In our research, we study the growth of diamond on carbide substrates and use the carbon already present in the substrate as the starting point for nucleation. This eliminates the need for a carbon deposition pre-treatment. The unique etching and growth chemistry of a $C_xF_y / H_2 / O_2$ plasma is responsible for diamond growth on carbide substrates, and this work builds upon the first reported work of the production of diamond films using CF_4 gas and microwave plasma on non-diamond substrates¹⁷. A model is proposed to explain the rapid growth of diamond on carbide substrates in the absence of a diamond powder pre-treatment.

EXPERIMENTAL

The samples were grown in a microwave plasma chemical vapor deposition system described previously¹⁸. A graphite susceptor is utilized to hold the substrate. No independent substrate heating is used; the plasma heats the substrate up to the required growth temperature. Table I lists the growth parameters.

The substrates used are reaction-bonded silicon carbide (RBSC) and tungsten carbide with 6% cobalt (WC / 6%Co) serving as a

binder. RBSC consists of small SiC particles bound together by a carbon binder. The outer edges of this binder develops a layer of silicon carbide, when exposed to gaseous silicon, that binds the silicon carbide particles together. Approximately 90 % of the sample is composed of the silicon carbide particles with the remainder the carbon binder. The WC / 6%Co is composed of tungsten carbide particles bound together by an interpenetrating network of elemental cobalt. This substrate is in the form of a tool insert (Ingersoll Cutting Tools Grade 110) approximately 2 cm in length by 1.5 cm in width.

Each substrate received its own unique surface preparation. For the RBSC, preparation consists of sectioning the rod (1 cm diameter) into 1 mm thick wafers and then polishing to a mirror-like surface finish with 600 grit SiC paper. Care was taken to ensure that the damage from the diamond impregnated sectioning wheel was completely removed from the sample. After the 600 grit polishing and rinsing with deionized water the RBSC disc was placed in the reaction chamber. The tungsten carbide surfaces of the tool insert were etched with a mixture of potassium ferricyanide ($K_3Fe(CN)_6$), sodium hydroxide (NaOH) and water in the ratio of 1:1:10 to roughen the surface. To remove the cobalt near the surface a 1:33 mixture of $FeCl_3$ and water served as the etchant. Exposure to the etchant for four hours removed the cobalt as determined by auger electron spectroscopy. After etching, the tool insert was rinsed in deionized water to remove any surface residue and placed in the growth chamber.

To examine the effect of fluorine on the growth of diamond a 5% F₂ in He and ultra high purity hydrogen gas mixture was used to treat RBSC substrates prepared as mentioned above. Experimental conditions for the pre-treatment are a pressure of 30 Torr, temperature of 525 C, microwave power of 300 W, gas flow rates of 8.8 sccm for the He/F₂ and 16 sccm for H₂. The fluorine treatment study consists of three different sets of experiments. In the first experiment, substrates are exposed to the He/F₂ gas mixture for ten minutes (H/F = 0), the gas composition is altered to the diamond growth conditions, and growth proceeds for two hours. Alternatively, substrates are exposed to the diamond growth plasma for two hours with He/F₂ added to this gas mixture (H/F = 500), or, in the third experiment, the substrates are pre-treated with He/F₂ and H₂ for ten minutes (H/F = 56) and then exposed to the diamond growth plasma for two hours. In no instance was the plasma extinguished when shifting from etching (pre-treatment) conditions to growth conditions.

Some explanation of the carbon source gas is necessary. The fluorocarbon gases shown in Table I were chosen specifically for their chemical and molecular structure. Figure 1 depicts each gas schematically and gives the bond strengths of the carbon-carbon and carbon-fluorine bonds. All of the gases are straight-chain molecules except for octafluorocyclobutane (C₄F₈) which possesses a cyclical configuration. The fluorocarbons containing two or more carbons are liquid phase (99% purity) with large vapor pressures at room temperature while the CF₄ is an electronics grade (99.995%)

gas. To characterize the diamond films, scanning electron microscopy (SEM) and Raman spectroscopy were performed.

For Raman spectroscopy the Ar⁺ 488.0 nm and 514.5 nm laser lines from a Spectra-Physics Model 2000 laser were used. The light was collected in a 180 backscattering geometry with no polarization of the scattered light before entering a Spex Model 1401 0.75 m double monochromator. Typical data collection is from 1000 cm⁻¹ to 1800 cm⁻¹ at a gate speed of 0.2 cm⁻¹/sec and a dwell time of 5 seconds.

RESULTS

A. Diamond Growth and Morphology

Figure 2 is a low and high magnification SEM micrograph of diamond growth for 1/2 hr. on the RBSC. The low magnification view shows a high density of crystallites on the surface that seem to cluster at particular locations on this RBSC surface. At a higher magnification, it is seen that the diamond is clustered (20 - 30 crystallites/particle) on the silicon carbide particles. The density of these crystallites is on the order of 10⁸ cm⁻² with a continuous film forming after approximately 2 hours of growth. The gaps between the carbide particles indicate where the carbon binder was before exposure to the plasma. The plasma species remove the carbon binder and no diamond is seen in the area previously occupied by this binder.

The evolution of surface morphology is seen in Figure 3. These SEM micrographs are of diamond grown with 3% CF_4 on RBSC for three different times. Nucleation occurs quite rapidly with the crystallites attaining a size of approximately 1.5 microns after 1/2 hr. of growth as shown in (a). Initially the crystallites are ball-like in nature with a uniform size distribution. This ball-like structure is to be expected when growing with high (3%) percentages of the carbon source gas. At 1 hour, the growth texture is starting to change as shown by the (100) facets forming on the now enlarged crystallites. The formation of a (100) texture is indicative of growth occurring fastest in the directions perpendicular to the (100) planes of the crystals. In this case, that would be growth velocities in the [111] and [110] directions¹⁹⁻²⁰. We also note the absence of secondary nucleation in Figure 3. Most of the impinging carbon is either being captured by the growing crystallites or is thermally desorbed; little is incorporated into the formation of new nuclei. After 6 hours of growth, well defined (100) facets, some with edges of 2-3 microns, are evident. The growth of faceted crystals at such a high carbon concentration is certainly unique to fluorocarbon gases. Hydrocarbons form only ball-like structures with a large percentage of non-diamond carbon at these source gas percentages. Apparently a more rapid carbon incorporation mechanism is occurring when diamond growth with fluorocarbon gases is used.

To prove the existence of diamond, the Raman spectroscopy results from the 6 hour film is shown in Figure 4. Only the broad

peak at 1332 cm^{-1} is seen, with little or no sp^2 bonded carbon present. Although not shown here, Raman spectroscopy results at the earlier growth times of one hour and 1/2 hour show the diamond peak at 1332 cm^{-1} , a graphite peak centered at around 1580 cm^{-1} and two peaks from beta-SiC at 970 and 790 cm^{-1} . Apparently, the growth of diamond is quite rapid in the early stages since one is able to see the diamond peak after only 1/2 hr. of growth.

Diamond growth can be generalized to other fluorocarbon gases and other carbide substrates. Figure 5 is a series of micrographs detailing the growth of diamond on RBSC using the fluorocarbon gases shown in Figure 1. All of the gases were used in the same volume percentages. The gases that contain 2 or more carbon atoms have relatively weaker carbon-carbon bonds compared to the C-F bonds. Molecular dissociation by electrons in the plasma would be expected to occur most rapidly at the weakest bonds (i.e. the carbon-carbon bonds). Consequently, more carbon is available to participate in the growth of diamond crystals and a larger nucleation rate should be seen. This type of behavior is exactly what is found experimentally. In Fig 5 (a), a widely spaced array of diamond crystals is seen with the rough underlying RBSC present. Figs. 5 (b), (c), & (d) depict the high density nucleation when utilizing hexafluoroethane (C_2F_6) (b), perfluoropropane (C_3F_8) (c), and octafluorocyclobutane (C_4F_8) (d). Carbon-fluorine atomic ratios range from 0.25 for CF_4 to 0.5 for C_4F_8 . This ratio determines the number of diamond crystallites that survive the nucleation stage and begin to grow into crystals. For the CF_4 case, the carbons are

outnumbered by the fluorines 4 to 1. Any carbon trying to form a nuclei on the surface has a high probability of being etched away by atomic fluorine. For C_4F_8 , there is a larger probability that the carbon atom trying to form a nuclei would encounter more carbon than in the CF_4 case. Statistics dictate that the nuclei have a better chance to survive and grow with more carbon present in the plasma.

Analogous growth behavior is seen when generalizing to other carbides, such as tungsten carbide. Figure 6 shows SEM micrographs of diamond growth on the WC/6%Co using the fluorocarbon gases listed previously. When growing with CF_4 , Fig 6(a), very small crystallites are seen with only a small portion of the sample covered by a continuous film. Figs. 6(b), (c), and (d) show continuous film formation with a slight decrease in the individual crystal size as one goes from (b) to (d) for the other fluorocarbon gases listed previously. Qualitatively, this set of micrographs is remarkably similar to the previous RBSC micrographs. This fact indicates that a similar reaction mechanism takes place on the surfaces of the two substrates. Elaboration of this mechanism is in the discussion section.

B. Effect of Fluorine on Diamond Growth

Previous work in our laboratory has shown that trying to grow diamond on WC / 6%Co and SiC substrates with 1/2% CH_4 resulted in no diamond formation. The only difference between the methane and

fluorocarbon growth plasmas is the presence of fluorine. Fluorine, whether it is in the atomic or molecular form, must be the controlling factor in the formation of diamond films on these two carbide substrates. To investigate the effect of added fluorine on the growth of diamond, a series of experiments was conducted involving the pre-treatment with fluorine before diamond growth, or the addition of fluorine during diamond growth with a 1/2% CH₄ plasma. The SEM micrograph results of this investigation are shown in Figure 7. Figure 7a is a micrograph of a sample grown with 1/2% CH₄ at the standard diamond growth conditions listed in Table I to serve as a control in the investigation. No diamond grows on the surface of the RBSC with a standard methane plasma known to grow diamond on diamond seeded silicon. As described previously, experiment 1 consisted of a ten minute pre-treatment with 5% F₂ in He gas mixture. The H/F ratio was 0. Figure 7b shows that no diamond grows on the surface. The second experiment investigates the effect of adding the 5% F₂ / He mixture to the diamond growth plasma. A micrograph of the resulting surface is shown in Figure 7c. Here the H/F ratio is 500. Again no diamond is found on the surface. Finally we use experiment 3 in which we combine 5% F₂ / He mixture with hydrogen in a H/F ratio of 56 for diamond growth. Under these conditions, we observe high nucleation density of diamond on the surface of the RBSC. The diamond crystallites are shown in Figure 7d. Large crystallites up to 5 microns in diameter are found in this photomicrograph. Texturing of the crystallites is also beginning to occur much like the texturing shown earlier in

the paper. This result is quite surprising indicating that the addition of hydrogen to the fluorine enables the diamond to nucleate. This finding will be discussed below.

C. Growth Mechanism

Thermodynamic arguments suggest that the etching of SiC can occur quite readily through atomic fluorine, CF_x species, and gaseous HF. Table II lists the reactions of interest as well as their free energy changes at 1200 K (the approximate growth temperature) calculated from JANAF thermochemical tables²¹. Immediately obvious is that all of these reactions have negative free energy changes with values ranging from -1405 kJ/mol to -342 kJ/mol. For etching with atomic fluorine, the production of silicon tetrafluoride (SiF_4) (Reaction 4) has twice the free energy change compared to the production of CF_4 (Reaction 5). Thermodynamics favors the production of SiF_4 over CF_4 implying that the removal of silicon from the silicon carbide is more favorable than the removal of the carbon from the silicon carbide. The etching of the SiC with CF_x radicals (reactions 1-3) also favors the production of SiF_x species. For etching with HF, surprisingly, the production of SiF_4 , and H_2 to expose a surface carbon atom is approximately as energetically favorable as the production of SiF_4 and CH_4 (reactions 6 -7) . We believe that the silicon is preferentially removed from the RBSC in the form of SiF_x ($x= 1-4$) leaving behind surface carbon atoms. These surface atoms have

minimum separation distances of 3.07 Å. This compares to the diamond lattice parameter of 3.56 Å with a minimum separation distance of 2.51 Å. Subsequent carbon containing species can then bond to the surface carbon atoms and begin the nucleation of the diamond. Growth occurs through standard hydrogen abstraction and radical addition proposed by other researchers.

Several reported works support this selective etching hypothesis. Suguira et. al.²² used mixtures of CF_4 and O_2 to reactive ion etch SiC thin films. When etching with this gas mixture, a carbon rich surface layer was found to form on the surface of the SiC. The auger peak intensity for carbon at the surface was found to be approximately three times the peak intensity of the silicon present on the surface. Since compounds tend to etch atomically, SiC etching can be viewed as the etching of Si and the etching of C with the Si etching faster resulting in carbon enrichment on the surface. From the large negative free energy changes listed in Table II, it is not hard to understand why the silicon is preferentially etched in the presence of fluorine and fluorocarbon radicals. Other researchers²³⁻²⁵ have seen the same type of behavior in their investigations of SiC etching. Palmour et. al.²³ investigated the dry etching of β -SiC single crystal thin films using CF_4 and CF_4 / O_2 gas mixtures. After exposure to a CF_4 plasma at a power density of 1.92 W/cm², the silicon peak corresponding to the LVV auger transition completely disappears indicating the presence of a carbon-rich surface. Other studies²⁶⁻²⁷ with diatomic chlorine gas show that silicon is also preferentially

removed from the silicon carbide matrix. The reaction probability for the formation of SiCl_4 is approximately four times higher than for the formation of CCl_4 resulting in the carbon-enriched surface.

A natural question to ask is why does diamond form at all. According to the thermodynamics espoused earlier, the carbon should etch just about as rapidly. The answer lies in the use of hydrogen for the growth of diamond.

Refer back to Figure 7. With a fluorine pre-treatment no diamond grows using CH_4 source gas. The pre-treatment with fluorine results in indiscriminate rapid etching of both the silicon and carbon in the silicon carbide most likely along the easiest etching planes of the SiC . Growth with CH_4 is precluded from the start since no surface carbon is exposed in any large quantity. Adding fluorine would be expected to increase the nucleation density of diamond by the selective etching mechanism; however, when the ratio of hydrogen to fluorine is 500:1, the amount of fluorine is too low to see the effects of the selective etching.

When pre-treating with a mixture of H_2 and F_2 with a H/F ratio of 56:1, the hydrogen serves to adjust the amount of highly corrosive atomic fluorine in the form of hydrogen fluoride. Enough atomic fluorine is then still available to selectively etch the silicon from the silicon carbide matrix leaving behind a carbon-rich surface. Nucleation of the diamond can proceed on this newly exposed surface carbon. The overall result is that the fluorine in the plasma must be controlled to enable the selective etching

mechanism to occur. A delicate balance needs to be maintained between the amounts of hydrogen and atomic fluorine in the discharge. Too much atomic fluorine causes over-etching while too little atomic fluorine results in no etching.

Tungsten carbide / 6% cobalt is believed to behave in a manner similar to the SiC described above. Tungsten readily forms volatile tungsten fluoride (WF) or tungsten hexafluoride (WF₆) when exposed to a CF₄²⁸ or CF₄ / O₂²⁹ plasma. The atomic fluorine in the discharge combines with the tungsten to produce these volatile fluorides. With the cobalt removed from the surface of the WC / 6% Co tool insert, only the tungsten carbide particles are exposed to the plasma enabling the preferential etching of the tungsten to begin. Residue leftover from the wet chemical etching of the tool insert are removed in the first five minutes, as determined by auger electron spectroscopy, and do not participate in the nucleation of the diamond crystals. The other fluorocarbon gases are believed to interact with the substrate in a manner similar to that described above; however, their reaction rate is much faster due to the additional fluorine atoms present in these molecules.

CONCLUSIONS

In summary, we have grown diamond on carbide substrates without any diamond pre-treatment and have provided a mechanism for

nucleation and growth. Continuous films approximately 3 microns thick formed after two hours of growth on both RBSC and WC / 6% Co. The initial stages of the mechanism involve the etching of the non-diamond component by atomic fluorine and concurrent growth of diamond nuclei. Etching involves the production of volatile fluorides that desorb from the surface leaving the carbon from the carbide matrix exposed to the plasma. Diamond growth starts on these surface carbon atoms and proceeds by standard abstraction and growth mechanisms. Hydrogen is essential in the growth process to control the amount of atomic fluorine available for etching. Excess fluorine upsets the delicate etching/growth balance and prevents the formation of any of the diamond phase. The process is insensitive to the type of fluorocarbon gas utilized and is expected to be applicable with any type of halogen containing gas.

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Table I. Diamond Growth Conditions

Substrate:	WC / 6%Co or reaction-bonded SiC
Surface Modification:	WC /6%Co: Chemical etch to remove Co and roughen WC particles SiC: No modification
Feed Gases:	CF ₄ , C ₂ F ₆ , C ₃ F ₈ , or C ₄ F ₈ all at 1/2% - 3%, 1% O ₂ , balance H ₂
Total Flow Rate:	200 sccm
Pressure:	40 mBar
Microwave Power:	350-400 W
Substrate Temperature:	900 C
Growth Time:	1-6 hrs.

Table II Abstraction Reactions

- | | |
|---|---|
| <p>1) $\text{SiC} + \text{CF}_4 \text{ ---> C-C} + \text{SiF}_4$
 $G_{\text{rxn}} = -629.8 \text{ kJ/mol}$</p> | <p>2) $\text{SiC} + \text{CF}_3 \text{ ---> C-C} + \text{SiF}_4$
 $G_{\text{rxn}} = -555.2 \text{ kJ/mol}$</p> |
| <p>3) $\text{SiC} + \text{CF}_2 \text{ ---> C-C} + \text{SiF}_2$
 $G_{\text{rxn}} = -341.9 \text{ kJ/mol}$</p> | |
| <p>4) $\text{SiC} + 4\text{F} \text{ ---> C} + \text{SiF}_4$
 $G_{\text{rxn}} = -1405.5 \text{ kJ/mol}$</p> | <p>5) $\text{SiC} + 4\text{F} \text{ ---> CF}_4 + \text{Si}$
 $G_{\text{rxn}} = -713.7 \text{ kJ/mol}$</p> |
| <p>6) $\text{SiC} + 4\text{HF} \text{ ---> SiF}_4 + \text{CH}_4$
 $G_{\text{rxn}} = -1058.2 \text{ kJ/mol}$</p> | |
| <p>7) $\text{SiC} + 4\text{HF} \text{ ---> SiF}_4 + \text{C} + 2\text{H}_2$
 $G_{\text{rxn}} = -1099.7 \text{ kJ/mol}$</p> | |

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Figure Captions

Figure 1. Structural schematic and bond energies for the fluorocarbons used in this study. Presented are the formulas, the structural arrangements, and selected bond energies of a) tetrafluoromethane, b) hexafluoroethane, c) perfluoropropane, and d) octafluorocyclobutane.

Figure 2. Detail of the diamond nucleation density on the silicon carbide particles, (a) low magnification, (b) high magnification.

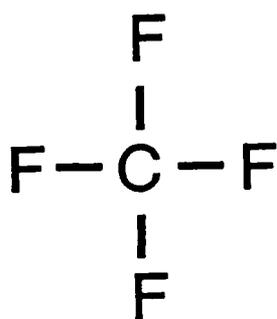
Figure 3. Evolution of the surface morphology of the diamond film on silicon carbide. (a) 1/2 hr., (b) 1 hr. (c) 6 hr.

Figure 4. Raman spectra of the continuous film shown in Figure 3(c).

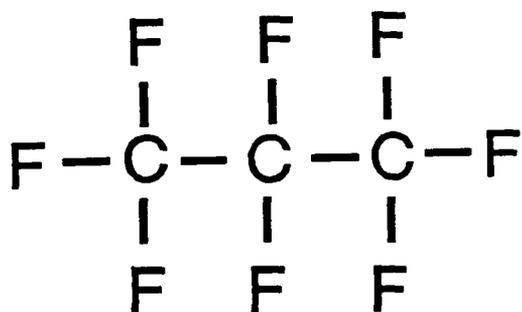
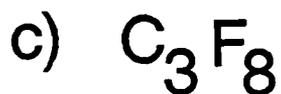
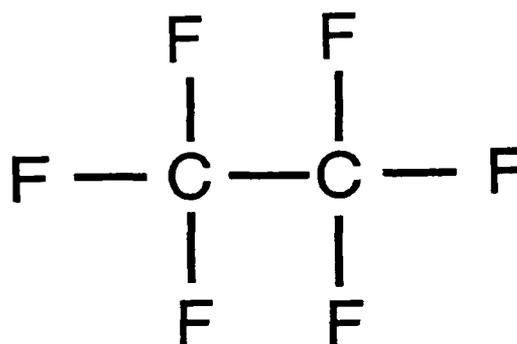
Figure 5. Growth of diamond on silicon carbide using various fluorocarbon gases. (a) 1/2% CF_4 , (b) 1/2% C_2F_6 , (c) 1/2% C_3F_8 , and (d) 1/2% C_4F_8 .

Figure 6. Growth of diamond on tungsten carbide / 6% cobalt using various fluorocarbon gases. (a) 1/2% CF_4 , (b) 1/2% C_2F_6 , (c) 1/2% C_3F_8 , and (d) 1/2% C_4F_8 .

Figure 7. Effect of fluorine on diamond growth on silicon carbide substrates. (a) no fluorine pre-treatment, growth with 1/2% CH_4 , (b) fluorine pre-treatment, H/F ratio: 0, growth with 1/2% CH_4 , (c) fluorine in during growth, H/F ratio: 500, growth with 1/2% CH_4 , (d) hydrogen/fluorine pre-treatment, H/F ratio: 56, growth with 1/2% CH_4 .



C-F 120 kcal/mol



C-C 69 kcal/mol

C-F 110 kcal/mol

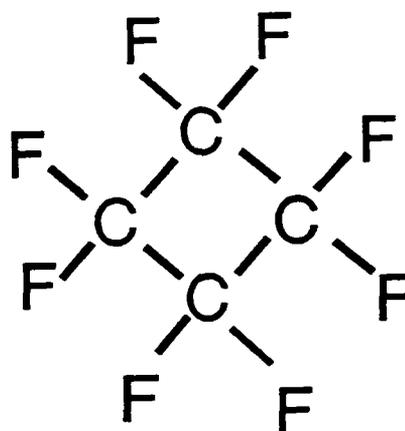


Figure 1

NOT AVAILABLE TO DTIC DOES NOT PERMIT FULLY LEGIBLE REPRODUCTION

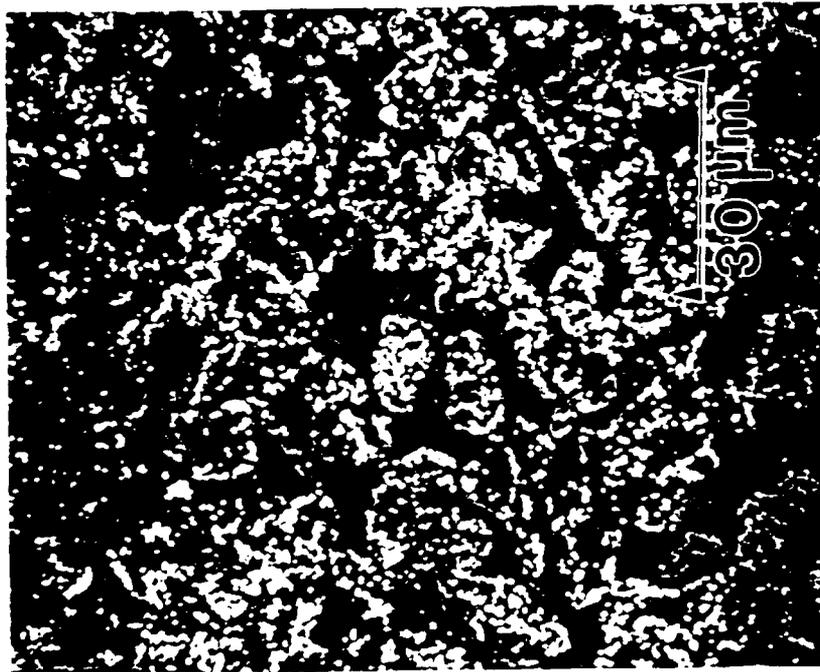
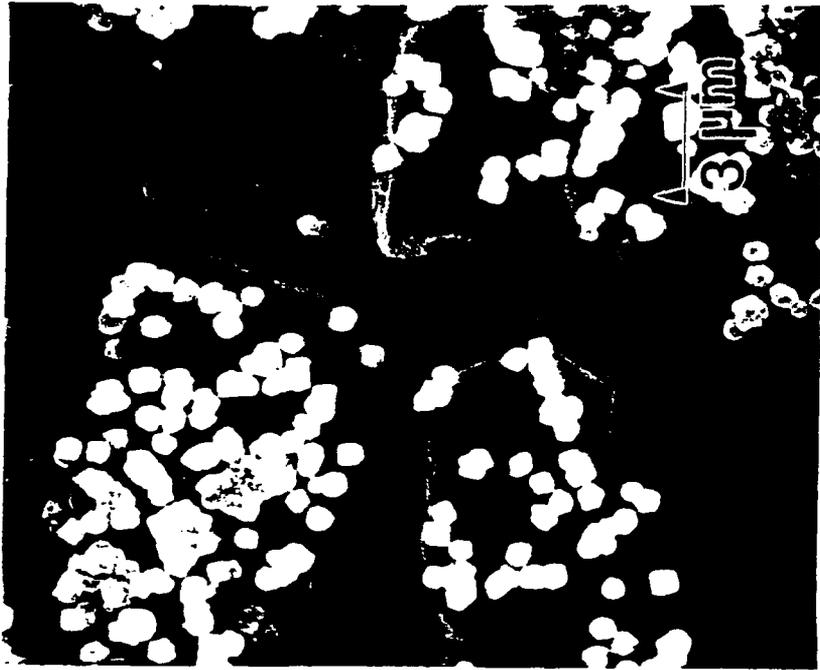
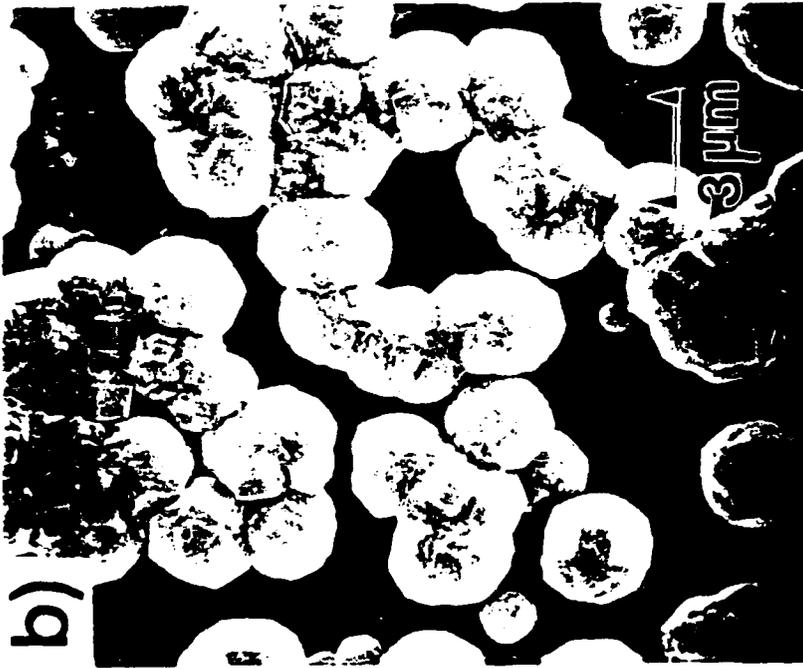
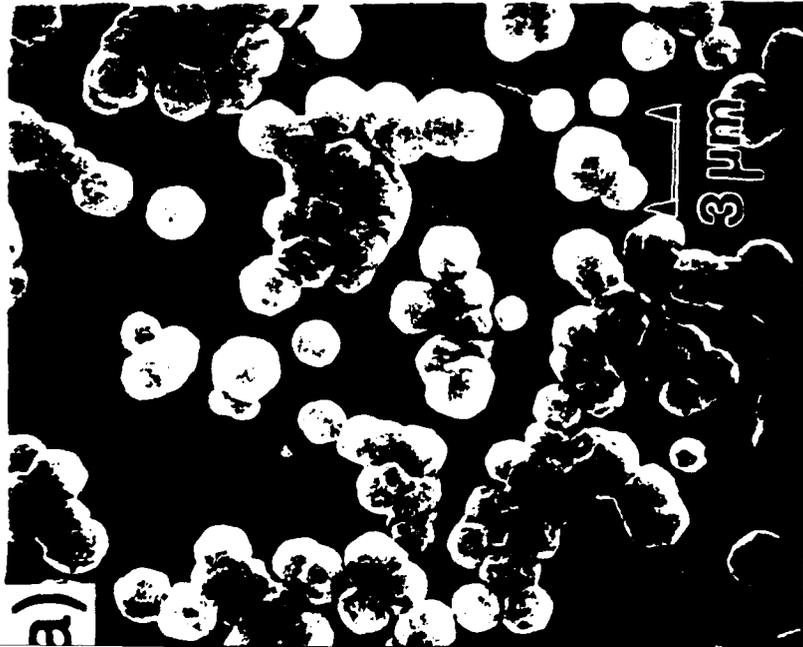
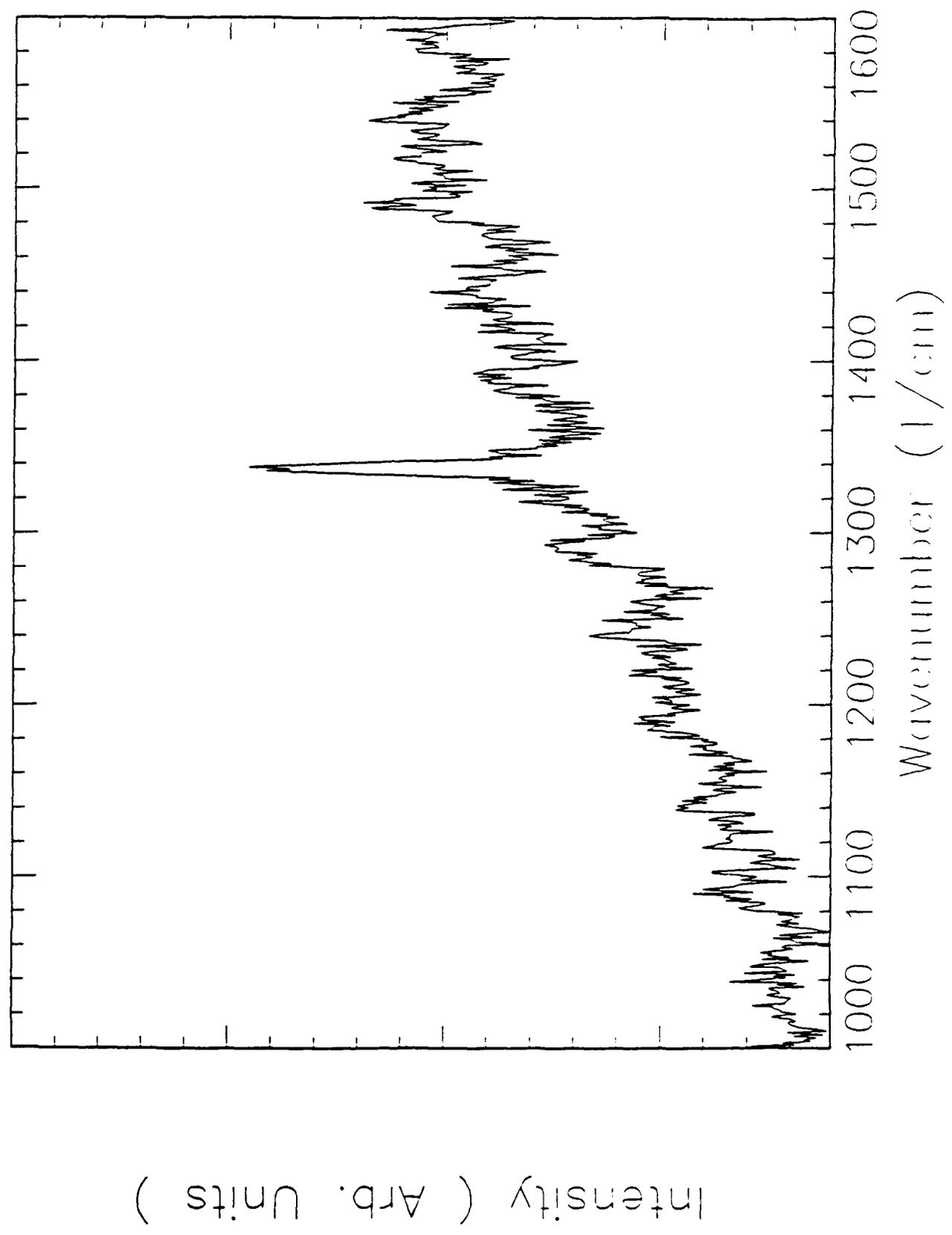


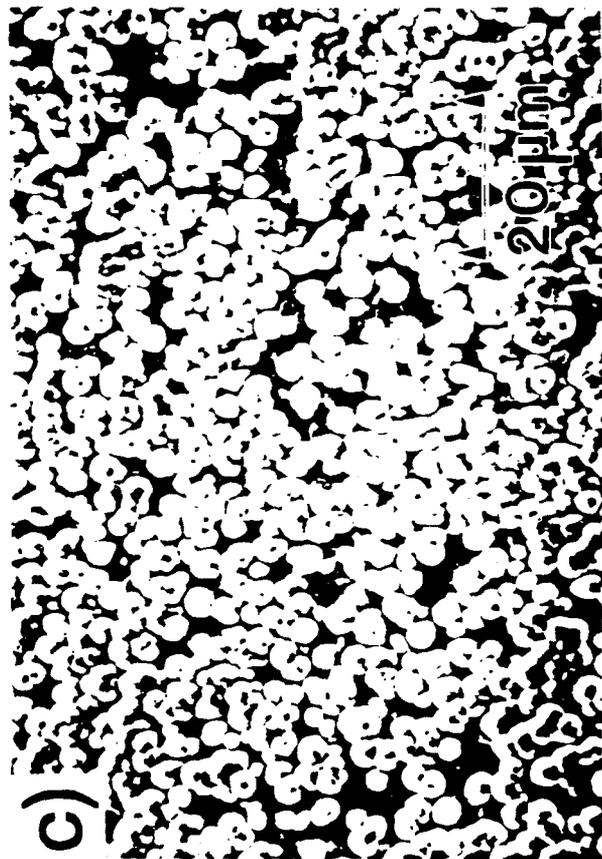
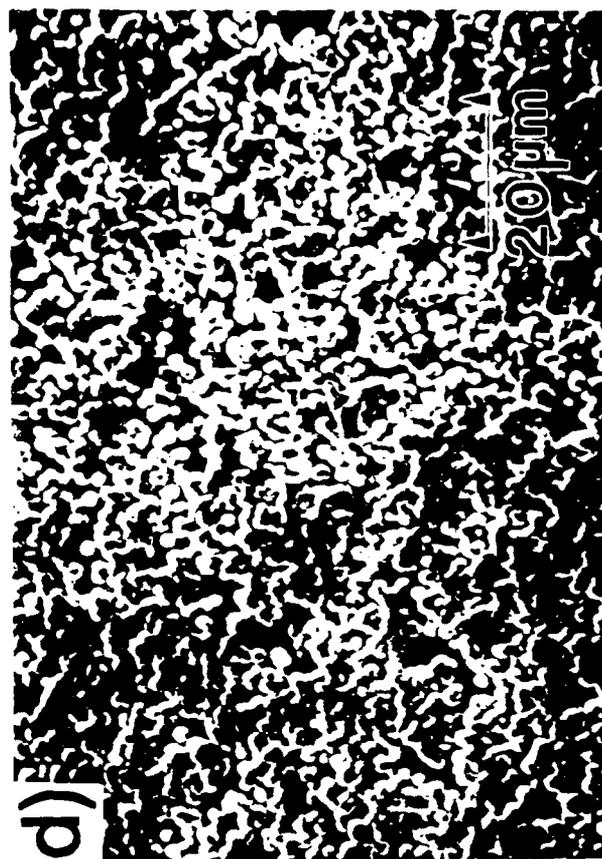
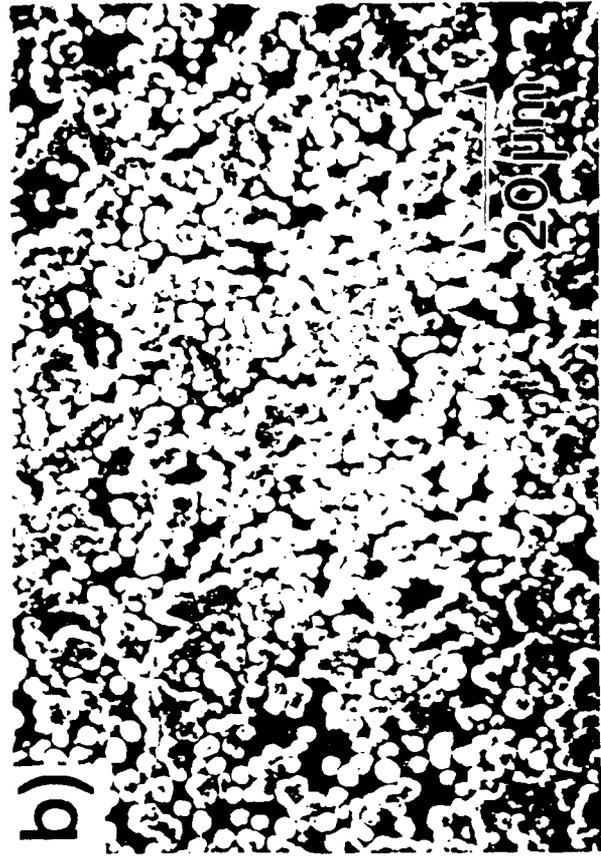
Figure 2



on SiC.

Figure 4





11/10/64

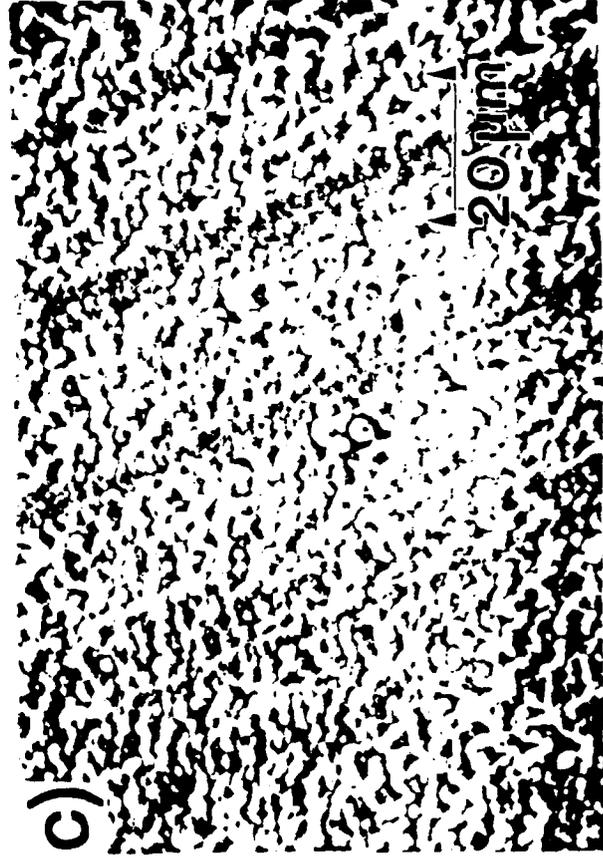
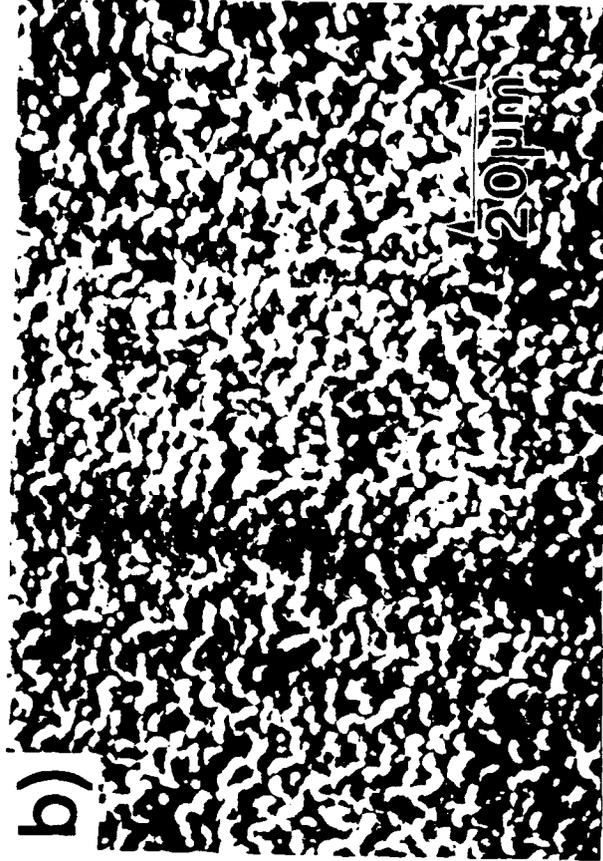
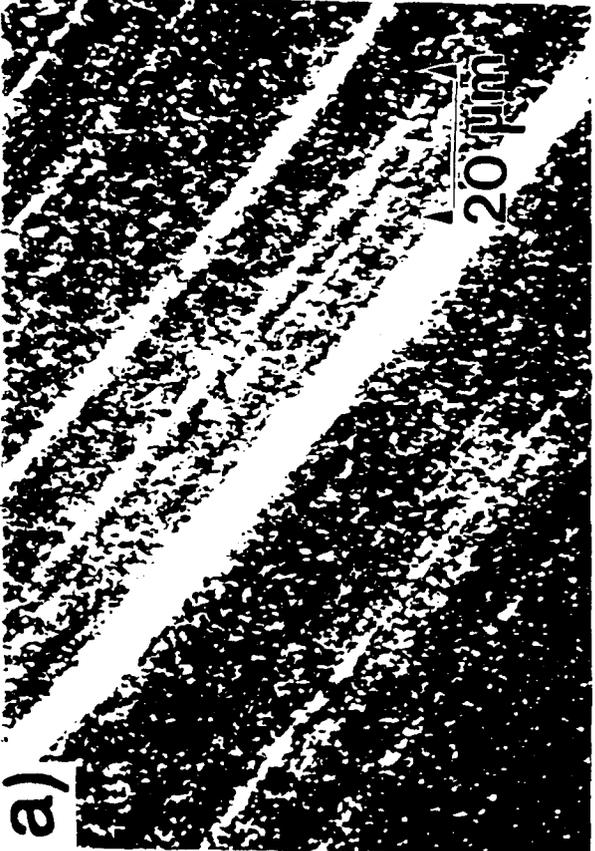
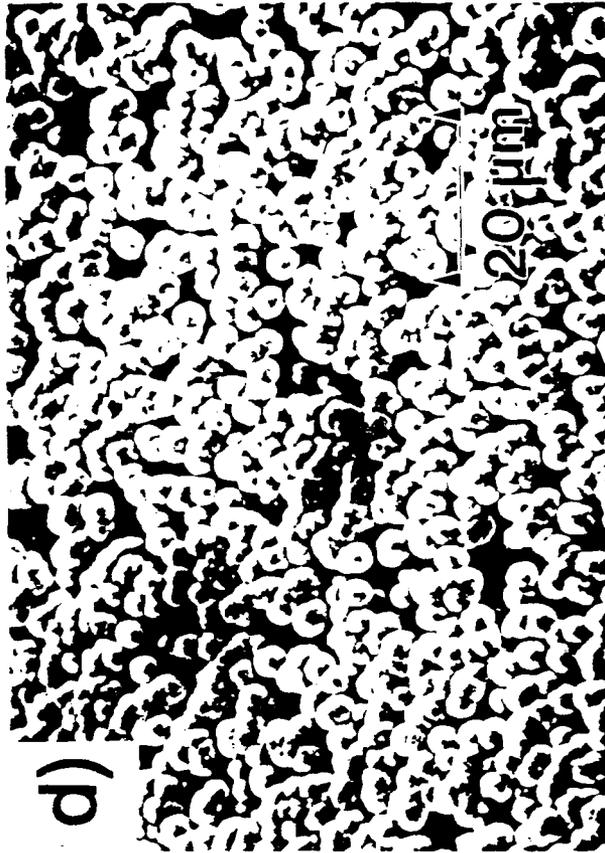
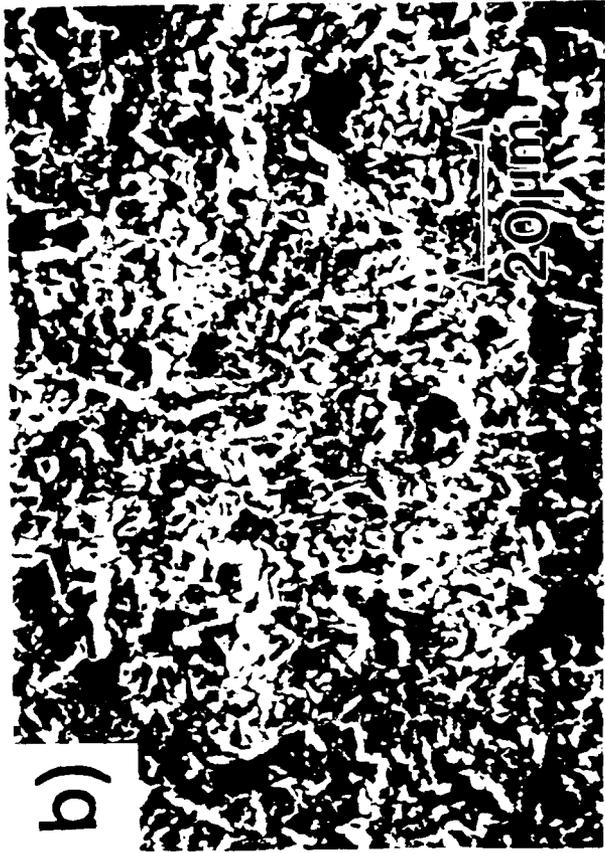


Figure 1



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