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THE STUDY OF CARBON-COATED GRIDS AT ELEVATED TEMPERATURES BY ELECTRON MICROSCOPY

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ABSTRACT

Copper, nickel, tungsten, gold and molybdenum microscope grids coated with thin carbon and SiO films were heated in a Hitachi electron microscope while being examined by both electron diffraction and electron imaging methods. Crystalline substances appear on the grids at various temperatures depending on the grid material. A comparison of the carbon-coated grids with the SiO coated grids along with other experimental evidence showed that two types of material were being formed on the carbon-coated grids. One substance was MoO_2 (coming from the specimen holder) while the other material is believed to be the various metal carbides.

INTRODUCTION

For a number of years, studies have been made on clay minerals and organic-clay complexes by means of heating-oscillating X-ray diffractometry. This is a method by which a specimen is heated in a X-ray diffraction apparatus, and the diffractometer tracing obtained while the sample is heated under a programmed rate to elevated temperatures. Based upon these studies, it was deduced that the morphology of these clay minerals and organic-clay complexes might change substantially while the sample was being heated. For this reason studies were undertaken to heat such samples to elevated temperatures in an electron microscope while studying the morphological and structural changes.

Studies by Furlong[1] on several clay minerals at elevated temperatures by electron microscopy have indicated that a particulate matter appeared on the clay surfaces, and associated with the clay at temperatures greater than approximately 500 °C. He concluded that the particulate matter that was being observed was coming from the clay mineral and was a result of the heating of these clays under the conditions of high vacuum in the electron microscope. For this reason we undertook to do similar experiments with our heating stage in an Hitachi HU11A electron microscope,

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but utilizing organic-clay complexes instead of the pure clay minerals previously used by Furlong. Shortly after these studies were begun, it was found that a carbon-coated copper grid could be inserted into the electron microscope and the same type of particulate matter would be formed in the absence of the clay or organic-clay complex. Based upon these results, it was decided to study the formation of this material in detail and to try to understand its origin.

EXPERIMENTAL

These investigations utilized the Hitachi HUIIA electron microscope equipped with a special heating specimen stage. Various electron microscope grids and coating materials were utilized in these studies as described below. In all of this work, the temperature of the coated grids was increased in step-wise increments allowing a minimum of 30 min at each temperature for thermal equilibrium to be obtained. This was necessary not only to allow the specimen to reach thermal equilibrium but also it was found to be very difficult to obtain well-focused pictures and electron diffraction patterns until instrumental thermal equilibrium was obtained. In some cases, the sample was left at a given temperature for as long as 2.5 h because particles of an interesting nature were being produced, or because unusual changes were taking place on particles already formed.

Five different types of grid were studied. They were as follows: copper grid–carbon film; nickel grid–carbon film; tungsten grid–carbon film; molybdenum grid–carbon film and gold grid–carbon film. For each of these grids, the temperature at which particulate matter could first be observed was determined, and then the morphological and electron diffraction patterns of the particles were determined up to temperatures as high as 700 °C.

Besides these grid–film combinations, studies were also made using grids with silicon oxide films. These grids were as follows: copper grid–SiO film; nickel grid–SiO film; tungsten grid–SiO film; molybdenum grid–SiO film; and gold grid–SiO film.

Electron micrographs and electron diffraction patterns were obtained in each grid–film combination. Depending upon the circumstances, both ring diffraction patterns and "spotty" diffraction patterns were obtained, although the ring patterns were by far the more prevalent. From the diameter of the diffraction rings, the corresponding *d*-spacings were calculated. The camera constant for the microscope was obtained under identical conditions of temperature and heating using aluminum or gold standards. On the average, the measured lines of the standards agree to within ±0.002 Å with the literature value of the *d*-spacings of aluminum and gold. Using the aluminum standard it was found that between room temperature and 600 °C the measured camera constant was changed by 0.38%. For *d*-spacings above 2.0 Å this change in camera constant produced a maximum variation of ±0.01 Å in the *d*-spacings from room temperature to 600 °C. Below 1.0 Å, the variation was no more than ±0.003 Å. Based upon the above experiments, the *d*-spacings given in the tables of this report are considered to be accurate to ±0.01 Å.

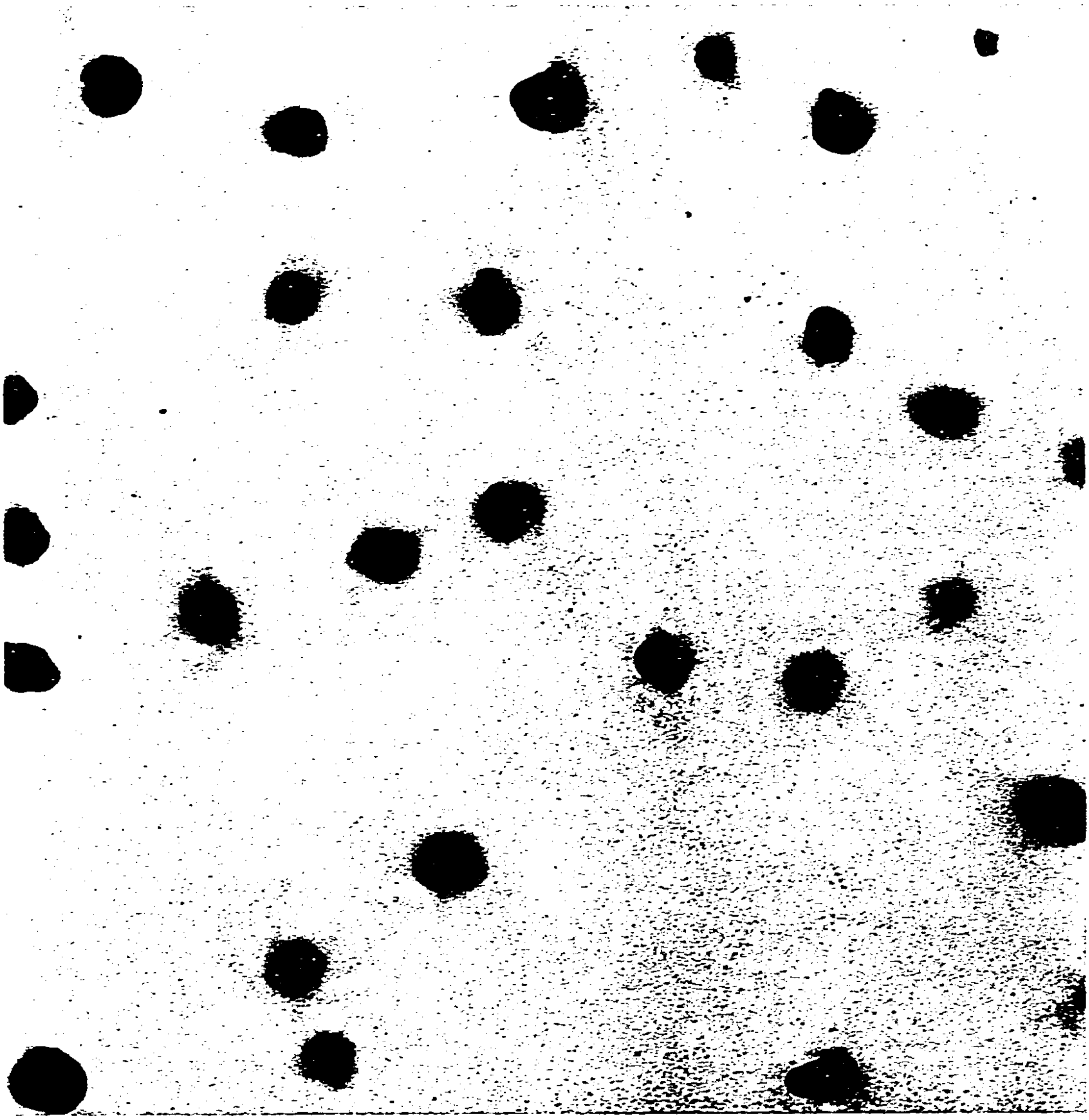
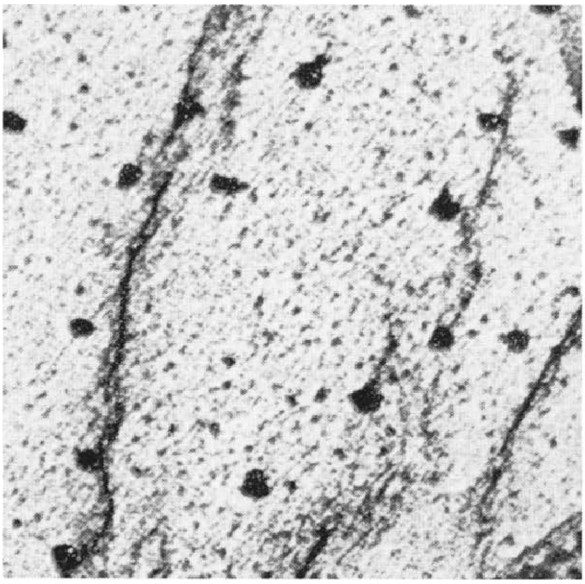


Fig. 1. Copper grid–carbon film, heated to 680°C for 1 h. Micrograph taken while heating; 12,375×.

RESULTS AND DISCUSSION

In the study of various types of metal grids coated with a thin film of carbon, it was found that there were differences from one metal to another with regard to the temperature that particulate matter could first be observed. There were also differences in the morphological appearances of the particles and in their electron diffraction patterns. The approximate temperatures at which particles were first observed to form (allowing 30 min at each temperature to reach equilibrium) are given in Table I.



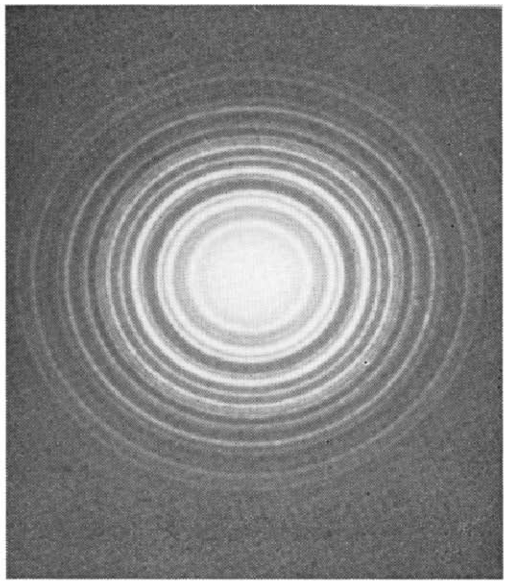
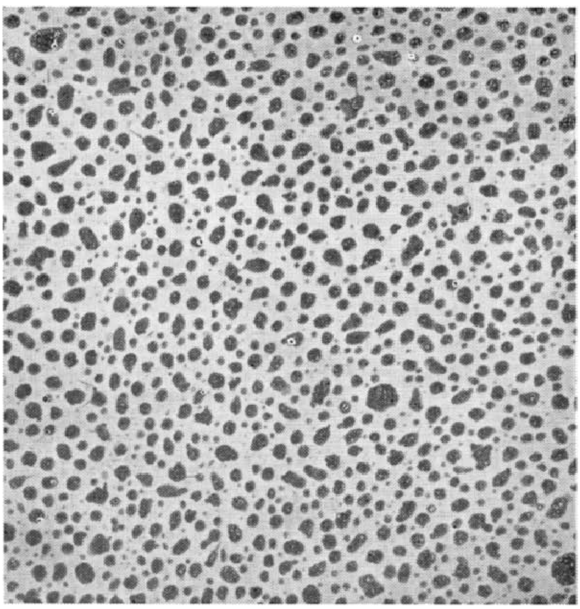


Fig. 2A. Nickel grid–carbon film, heated to 690 °C for 2 h. Micrograph taken while heating; 6,040 ×.

Fig. 2B. Nickel grid–carbon film, heated to 690 °C for 2 h. Diffraction given by area in Fig. 2A. Taken while heating.



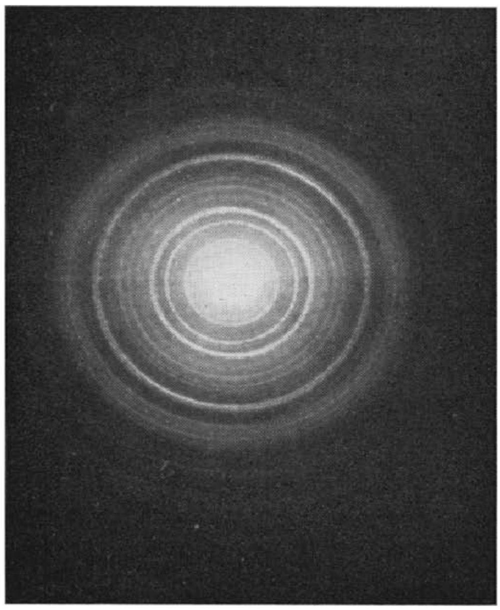


Fig. 3A. Tungsten grid–carbon film, heated to 650 °C for 30 min. Micrograph taken while heating; 4400 ×.

Fig. 3B. Tungsten grid–carbon film, heated to 650 °C for 30 min. Diffraction given by area in Fig. 3A. Taken while heating.

TABLE I

TEMPERATURES AT WHICH PARTICULATE MATTER WAS FIRST OBSERVED FOR VARIOUS TYPES OF GRID

Type of grid	*Temperature (°C)*
Copper	400
Nickel	600
Molybdenum	500
Tungsten	550
Gold	500

Some of the more pronounced differences in the morphology and electron diffraction patterns for the carbon-coated grids are illustrated in Figs. 1–6.

Fig. 1 illustrates the morphology for a copper grid with a carbon-coated film, heated to 680°C for 1 h. Fig. 2A and 2B show the electron micrograph and the electron diffraction pattern, respectively, obtained for a carbon-coated nickel grid when heated to 690°C for a 2-h period. Figs. 3A and 3B illustrate the type of morphology obtained with a carbon-coated tungsten grid and its respective electron diffraction pattern. This particular sample was heated to 650°C for a 30-min period. In order to illustrate some of the properties of the particulate matter that was formed, Fig. 3A might be compared with Fig. 4, which is another picture of a carbon-coated tungsten grid, but this time heated to a lower temperature of 550°C. It should be noted that in these particular pictures, there are somewhat different morphological characteristics of many of the particles. In Fig. 4, the particles appear to be of two distinct types, the small angular material and the sheet-like material that in many instances is rolling up into rod-like material.

A carbon film on a gold grid is illustrated in Fig. 5A along with its diffraction pattern, shown in Fig. 5B. Finally, Figs. 6A and 6B illustrate the type of particles obtained, and the electron diffraction patterns for a carbon-coated molybdenum grid.

If one carefully examines the diffraction lines obtained in the case of the carbon film grids, there are found to be a number of lines which are common to every type of metal grid and always appear. However, in addition to these common lines, for each type of metal grid used there are at least six additional lines which are quite different and not common. For tungsten there are a number of such lines. In explaining the common lines, it was felt that a contaminant was involved coming from some part of the microscope system.

The particulate matter being formed and giving rise to the common diffraction lines is molybdenum oxide, MoO_2, as determined by the electron diffraction patterns and comparing them with the *d*-spacings of standard ASTM patterns. In the case of grids other than molybdenum the diffraction lines that are seen over and beyond the molybdenum oxide lines have not been completely identified, but it is believed that they are diffraction lines belonging to the various respective metal carbides.

In order to determine if the material was indeed molybdenum oxide and in

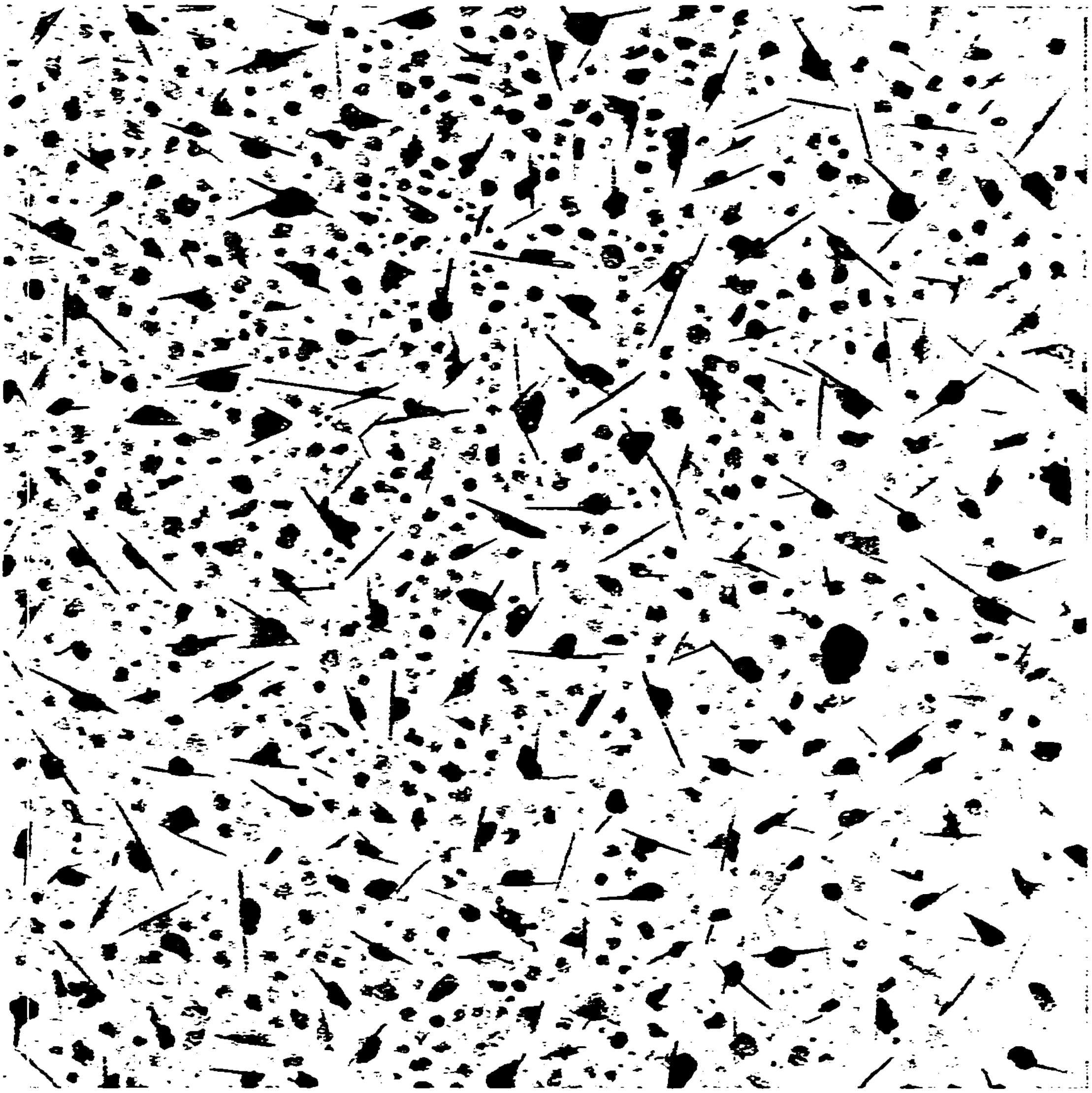
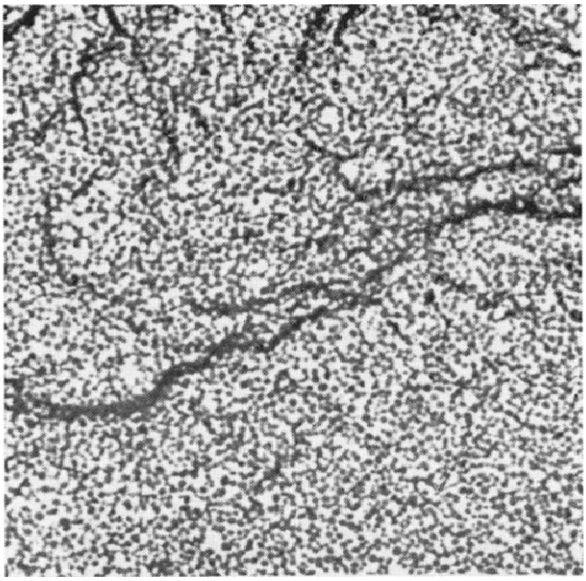


Fig. 4. Tungsten grid–carbon film, heated to 550 °C for 1 h. Micrograph taken while heating: 16,500 ×.

order to try and determine where this material could be coming from in the samples with grids other than molybdenum a number of experiments were run. The small cylindrical holder which is in actual contact with the electric heating device was found to be made of molybdenum metal. It was immediately suspected that the source of the molybdenum which in turn formed the molybdenum oxide would be the molybdenum holder. After repeated use, the holder was seen to have a violet-brown coating formed over the molybdenum metal. This is the color of MoO_2. The holder was placed in a vacuum evaporator in a tungsten basket and heated to orange-white heat. The violet-brown coating was completely removed, presumably through volatilization of the molybdenum (IV) oxide. Very recently, a tungsten grid with a carbon film was



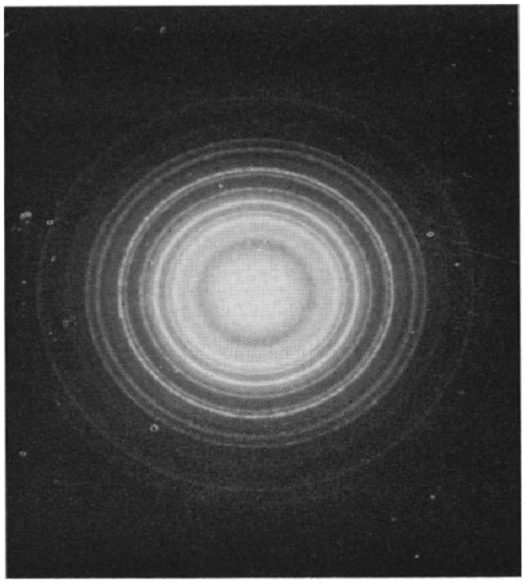
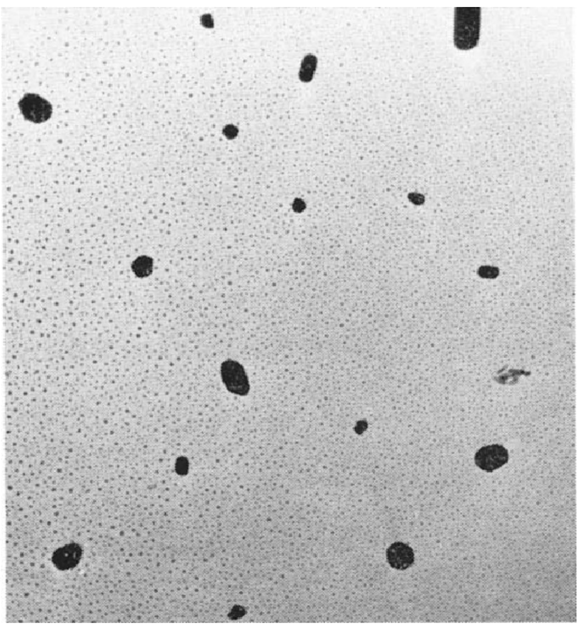


Fig. 5A. Gold grid–carbon film, heated to 720 °C for 1 h–30 min. Micrograph taken while heating; 9880 ×.

Fig. 5B. Gold grid–carbon film, heated to 720 °C for 1 h–30 min. Diffraction given by area in Fig. 5A. Taken while heating.



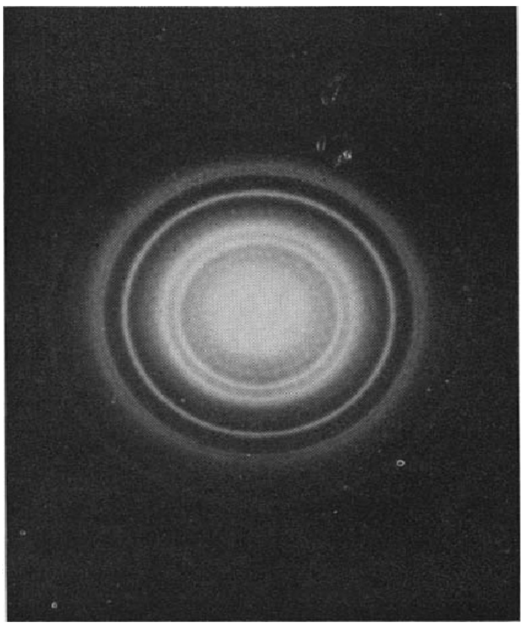
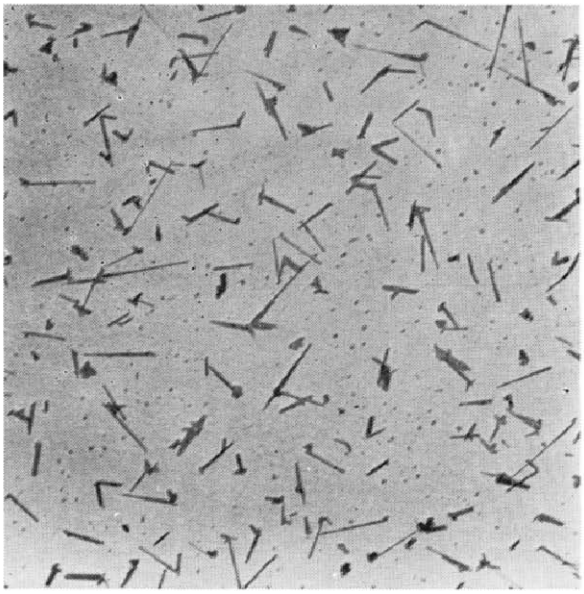


Fig. 6A. Molybdenum grid–carbon film, heated to 710 °C for 1 h. Micrograph taken while heating; 3280 ×.

Fig. 6B. Molybdenum grid–carbon film, heated to 710 °C for 1 h. Diffraction given by area in Fig. 6A. Taken while heating.

heated to 700°C using this decontaminated specimen holder. The rod-shaped particles characteristic of MoO_2 were not observed and neither were any of the common diffraction lines obtained. However, the dense angular particulate matter was observed and all of the previous diffraction lines not attributable to MoO_2 were obtained. It was concluded, therefore, that the source of this contaminant was indeed the molybdenum holder. This same result has recently been verified using a copper grid and carbon film.



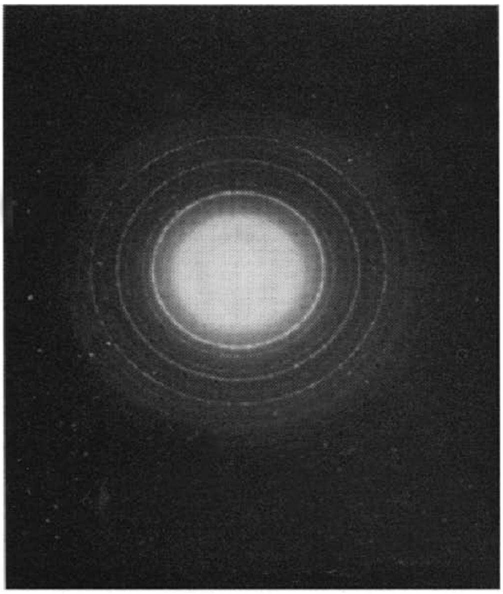


Fig. 7A. Molybdenum grid–SiO film, heated to 585°C for 45 min. Micrograph taken while heating; 9000×.

Fig. 7B. Molybdenum grid–SiO film, heated to 710°C for 30 min. Diffraction given by area in Fig. 7A. Taken while heating.

It was now necessary to see if further information could be obtained with regard to the other type of particulate matter being formed on the girds. In this case, it was found that this other material was sensitive to the particular temperature at which the grid was being heated and to the type of grid being used. For these studies all of the grids previously used were prepared with silicon oxide films replacing the carbon films. Since it was suspected that the particles being formed were carbides of the various grid metals it was felt that by replacing the carbon film with silicon oxide film, the formation of the carbide could be prevented. Figs. 7A and 7B illustrate a typical type of electron micrograph and electron diffraction pattern obtained with SiO-coated grids. This particular grid was a molybdenum grid coated with the SiO film. As with all grids when coated with SiO, only one very distinct electron diffraction pattern was obtained, as illustrated in Fig. 7B. By comparison of the diffraction pattern with standard ASTM card index it was readily shown that the material being formed was molybdenum oxide, MoO_2. A further illustration of this is shown in Fig. 8,

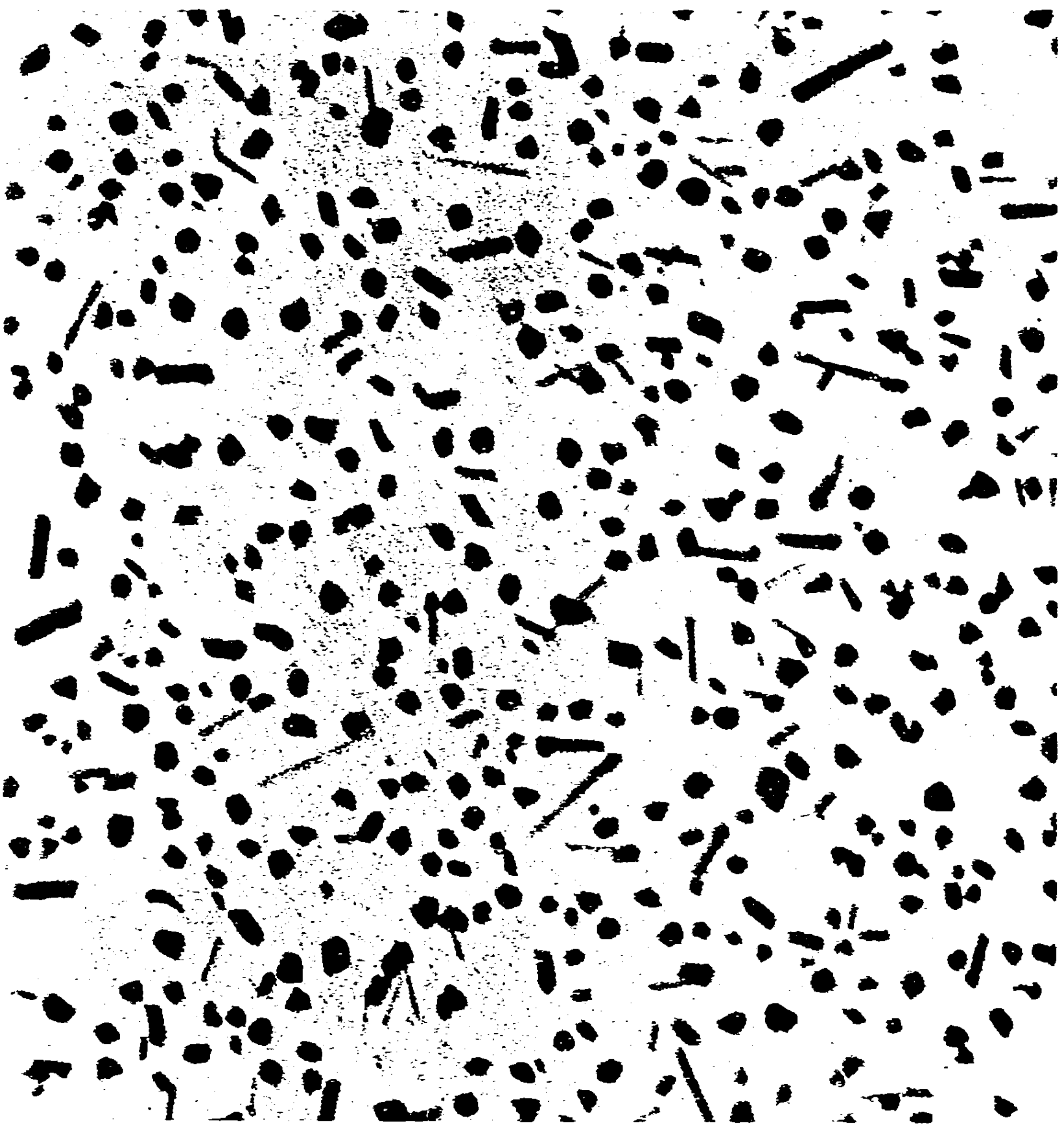


Fig. 8. Copper grid–SiO film, heated to 720 C for 30 min. Micrograph taken while heating; 21,225 ×.

which shows the electron micrograph for a silicon oxide coated copper grid and a standard molybdenum holder. In all silicon oxide coated grids the diffraction patterns were identical, which further showed that the contaminant material was coming from a source other than the grid and from the carbon film. From these micrographs it was again confirmed that the contaminant particulate material comes from the molybdenum holder and not from the grid material. It further illustrates that the particulate matter observed in the carbon-coated grids other than the molybdenum oxide is indeed a function of the carbon film, and, therefore, is very probably a metal carbide, since no other change was observed besides the deposition of the contaminant. Since the noncommon diffraction lines obtained in the various patterns are different when one goes from one grid to another, it is reasonable to conclude that it is not just molybdenum carbide being formed but very likely a carbide of the grid material reacting with the carbon film.

If one goes back and studies the electron micrographs very carefully, it will be observed that in many instances the particles being formed are being formed in an area where the carbon film appears to be disappearing. This is evident by noticing that around many of the particles the thickness of the carbon film is less than that in other areas by virtue of the fact that the electron beam more readily transmits through that particular area. Fig. 9 shows a Ni-grid with carbon coating heated to elevated temperatures, in which the carbon films has been degraded in the area where the film is rolled back on itself. It is believed, therefore, that this is further evidence of the metal reacting with the carbon to form the particulate carbide.

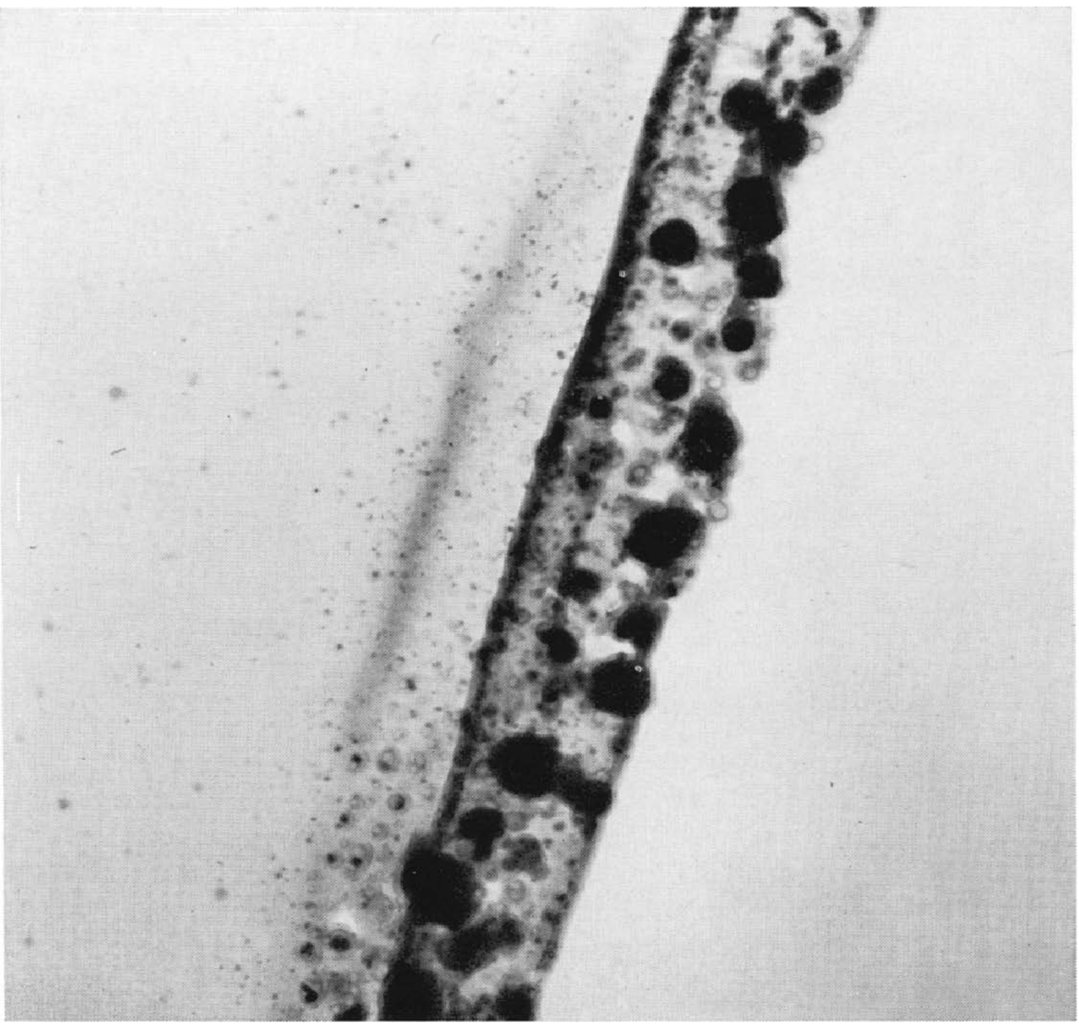


Fig. 9. Nickel grid–carbon film, heated to 630°C for 2 h. Micrograph taken while heating; 32,250×.

Table II gives the electron diffraction data for the various carbon-coated grids used in this study, along with the d-spacings of lines obtained for the various grids with silicon oxide films. The d-spacings with an asterik in the Table are those lines that are attributed to the molybdenum dioxide portion of the pattern. The lines without an asterik are, therefore, believed to be the lines belonging to the metal carbide. Lines of these possible carbides compared with the ASTM data file do not give an exact match. However, it was observed that in some instances, several of the reported carbides would fit the data if mixtures were assumed. Since all of these metals form

TABLE II

SELECTED-AREA ELECTRON DIFFRACTION DATA

Carbon-coated grids (d_{hkl} – Å)					*SiO-coated grids* (d_{hkl} – Å)
Copper	*Nickel*	*Molybdenum*	*Tungsten*	*Gold*	*Avg. of all types*
			5.10		
			4.17		
	3.38*		3.75		3.41
			3.26		
			3.06	3.05	
		2.91	2.95		2.82
	2.77		2.71		
			2.67	2.45*	2.44
	2.43*	2.45*	2.44*	2.34	
2.11	2.14	2.08	2.05	2.16	2.18
			1.91	1.93	
1.82*	1.83*		1.84*		1.84
	1.70*	1.70*	1.68*	1.68*	1.73
	1.52		1.62		1.54
		1.47		1.48	
	1.46		1.41*	1.42*	1.41
	1.40*		1.37		
	1.34		1.33	1.30*	1.31
1.30*	1.29*	1.26	1.24*	1.22*	1.21
	1.21*	1.20*			
			1.17	1.14	
	1.17	1.03*	1.12*	1.080*	1.12
1.10*	1.077*		0.999	1.045*	1.090
	1.029*		0.985	1.020	1.036
		0.947	0.940	0.924*	0.920
		0.927*		0.891	
	0.910		0.831		0.859
	0.874	0.848		0.858*	
			0.814	0.827	
0.840	0.850	0.796			
0.817			0.791		
0.746			0.756		
		0.692		0.664	
0.698	0.660		0.633		
			0.623		

many different carbide modifications it is very possible that mixtures would be obtainned and, therefore, with the limited amount of diffraction lines obtained, that exact matches could not be made. A reasonably good fit is obtained with the tungsten grid lines and a $M_{23}C_6$ face-centered cubic carbide.

Both Laird[2] and Ansell and Aaronson[3] have described the technique of hot-stage transmission electron microscopy and the criteria for its use. However, it is concluded that when a heating stage in electron microscopy studies is utilized, one should be aware of the possibility that carbides can be formed under the normal conditions of operating the electron microscope. Therefore, for those wishing to perform electron microscope studies at elevated temperatures, films other than carbon should be used. Also, if the standard type of molybdenum holder is being used, this holder should be treated as mentioned so that the molybdenum oxide particulate matter that was observed in these studies will be eliminated.

ACKNOWLEDGEMENT

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