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NEW COMPLEX TRANSITION METAL CARBIDES FORMED ON AN ELECTRON MICROSCOPE HEATING STAGE

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ABSTRACT

Particles shown to be complex carbides of copper, nickel, molybdenum, tungsten, gold, silver and titanium along with carbides of the elements in stainless steel, were formed on an electron microscope heating stage. These particles were observed to form on thin carbon films coating the electron microscope grids of the metals listed above. The d-spacings measured for these particles are essentially the same as those that are observed with a mixture of the complex carbides of general formula M_6C and $M_{23}C_6$. Electron microprobe analysis was performed on the particles formed in the microscope, and the analysis confirmed the presence of the respective metals within the particles. In general, the various metal carbides were observed to form at different temperatures on different metal grids.

INTRODUCTION

In an earlier report[1] in this Journal, evidence was given that metal carbides of the elements copper, nickel, molybdenum, tungsten, and gold were formed on the heating stage of a transmission electron microscope by reaction of metal from the microscope grid with the thin carbon film coating the grid. Further investigation has been made of this reaction in order to more fully understand the nature of these reaction products and to study additional metals. Evidence obtained here for the formation of carbides of copper, silver, and gold represented a new development in carbide chemistry since for binary systems, no stable carbides of copper, silver, and gold have been reported[2–7]. In a ternary system of two or more metals plus carbon, no carbides containing silver and gold have been reported[6,8], and in only one instance[9] has there been a report of carbides formed containing copper which was present as a minor constituent.

Not only were the conditions of formation of the carbide particles studied in more detail, but the presence of the metals comprising the various microscope grids were demonstrated to be present in the particles formed on the thin-film carbon coating by the use of electron microprobe analysis.

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Fuschillo et al.[10] carried out a similar heating study using a copper grid coated with a thin film of carbon. These workers observed particles to form on the carbon film at elevated temperatures and from their diffraction data suggested that the particles were highly crystalline graphite. As will be more evident later, the same conclusions cannot be drawn from the work reported herein.

EXPERIMENTAL

The experimental techniques used in this study have been described previously[1]. The Hitachi HU-LLA electron microscope equipped with a special heating stage allowed the sample to be heated to temperatures as high as 800 °C, and to be viewed at these temperatures under continuous heating conditions for an indefinite period of time. Both electron micrographs and selected-area electron diffraction patterns could be taken at elevated temperatures with continuous heating under these circumstances.

Control of the temperature of the sample on the heating stage and obtaining accurate values for the d-spacings of the carbide particles formed were crucial to the conclusions of this study, and consequently, much effort was expended in evaluation of these parameters. For a given value of heater current, the final equilibrium temperature obtained in the molybdenum microfurnace was found to be reproducible to ± 5 °C. Also, by observation of the actual melting of known materials deposited on the carbon coated grids (e.g. aluminum metal), the recorded temperatures were found to be accurate to ± 10 °C. As in all previous work, the electron micrographs and selected-area electron diffraction patterns were recorded only after the sample had been held at a particular temperature for 30 minutes. This was sufficient time to allow the sample to reach thermal equilibrium.

In order to compare temperatures at which the various carbide particles were formed on the metal grids, a standard heating procedure was followed. The formation temperatures listed in Table 1 were obtained by the following heating procedure:

> The sample was heated from room temperature to 400 °C in approximately one hour, where it was then allowed to remain for the 30 minute equilibration time. This temperature was chosen as the starting point because this was the lowest temperature at which particles could be observed to be formed after a 30 minute waiting period. After holding the samples at 400 °C for 30 minutes, the samples were heated as quickly as possible to successively higher temperatures in 50 °C intervals. By this uniform heating procedure, each type of grid was studied to determine at approximately what temperature particles on that particular metal grid could be visibly observed to form. Although the procedure was somewhat arbitarary, it did make possible a useful comparison among the various samples. Once the formation temperature was obtained for a particular grid, a number of additional studies were performed in which samples were heated to a particular temperature of interest for times up to six hours.

TABLE I

APPROXIMATE FORMATION TEMPERATURES OF CARBIDE PARTICLES FORMED ON CARBON FILM COATED GRIDS UNDER CONTROLLED HEATING CONDITIONS

Metal grid	*Temperature of formation (°C)*
Copper	400
Nickel	600
Molybdenum	500
Tungsten	550
Gold	500
Silver	600
Titanium	550
Stainless Steel	600

The accuracy of electron diffraction measurements made while heating at elevated temperatures was evaluated by measuring the diffraction patterns of known materials (e.g., aluminum and gold) at elevated temperatures, and then by making comparison of these experimentally obtained d-spacings with reported values. Based on such measurements, the following limits of accuracy are placed upon the d-spacings reported. Above a d-spacing of 4.0 Å, the values are accurate to ± 0.1 Å because of the small diameters of the lines, and because of the "fogging" effect of the non-diffracted central electron beam. From a d-spacing of 3.0 Å down to 2.0 Å, the d-spacings are accurate to ± 0.02 Å, although a weak line may have slightly more uncertainty. Between 2.0 and 1.0 Å the values of the d-spacings are certain to ± 0.01 Å, and below 1.0 Å the values are accurate to ± 0.005 Å.

Qualitative analysis for the presence of metallic elements within the carbide particles formed on various types of grids was performed by means of electron microprobe analysis carried out on a Cambridge Steroscan (Mark 2A) SEM. A 20 kV accelerating voltage was used in all cases, and X-ray photon excitation was produced within single carbide particles because a narrowly defined 100 Å diameter electron beam was produced. The X-ray photons produced were analyzed by means of an energy dispersive solid state detector (a lithium drifted silicon semiconductor) with the energy calibration from 0 to 10 keV. This particular system had a detection limit of 10^{-16} grams or ten parts per million (10 ppm) on a solid solution basis. Because of limited availability of instrumental time, no specific attempts were made to quantitatively determine the amount of any element present, although some qualitative comparisons were made.

DATA AND RESULTS

Figures 1–8 are representative electron micrographs of particles formed on the carbon films coating the various metal microscope grids. Figures 9 and 10 are typical selected area electron diffraction patterns given by particles formed on the carbon

films of the grids. Except for Figs. 5 and 6, all of these figures represent results obtained while the sample was heated to the elevated temperature indicated.

An examination of Figs. 2–8 reveals that the carbon films coating the respective grids appeared to have been degraded or "consumed" as a consequence of the formation of particulate matter. In almost every instance, the degree of film degradation was most pronounced in an area where larger particles were seen to be formed.

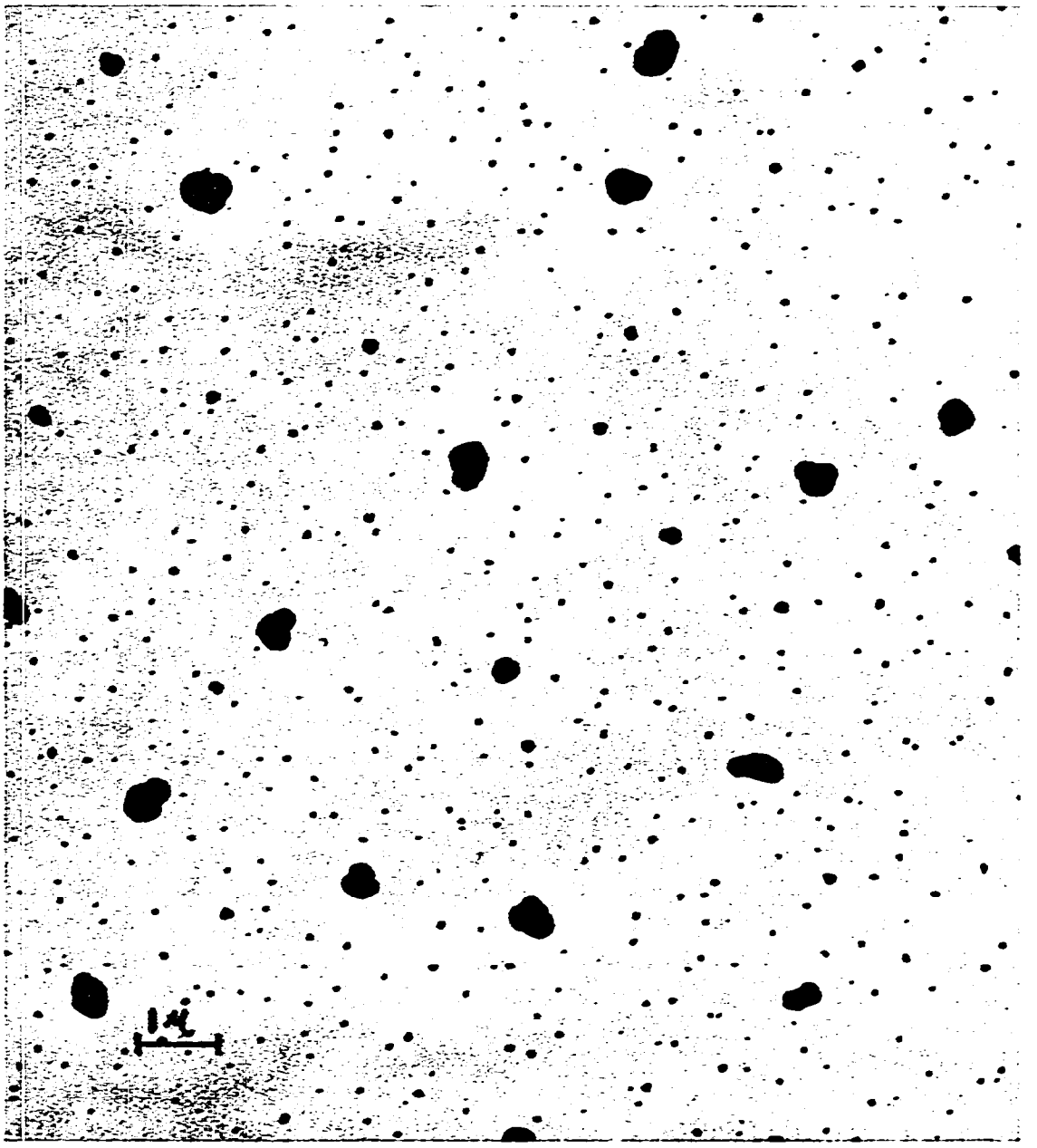

Fig. 1. Electron micrograph of particles formed on a copper grid with a carbon thin-film coating heated to 690 C for 30 minutes. Picture taken during heating cycle. Magnification, 9700×.

Figure 4, for example, shows particle formation along and within an area where the carbon film had become folded back on itself. Prior to heating the sample, a sharp edge was observed along the fold, while after heating a jagged edge was seen suggesting extensive film degradation.

The electron micrographs revealed that there were variations in both particle

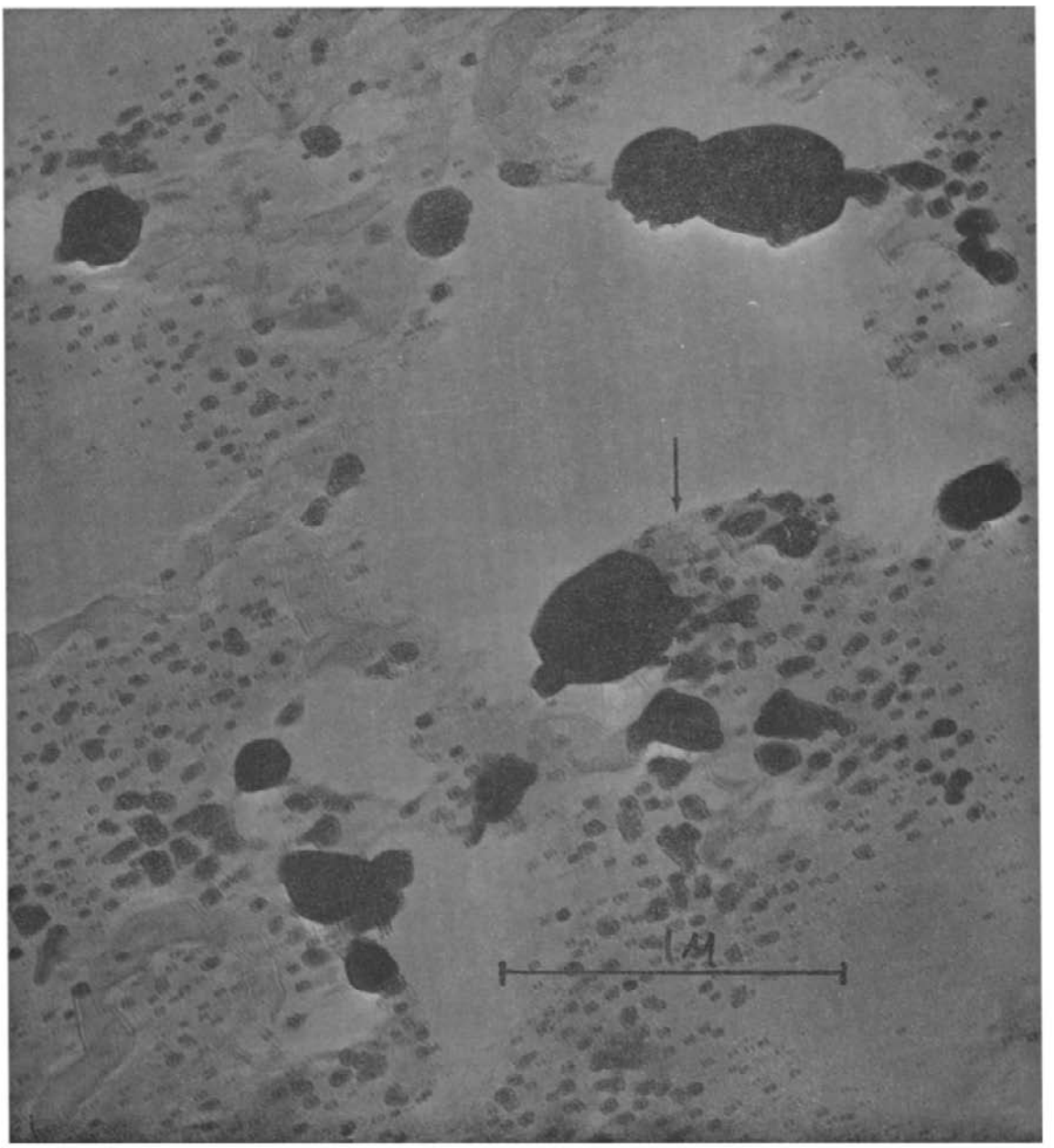

Fig. 2. Electron micrograph of particles formed on a silver grid with a carbon thin-film coating heated to 700 °C for 2 hours. Picture taken while heating. Magnification, 41 100×. The arrow points to an area where the carbon film has been degraded.

size and particle density on any heated sample. Furthermore, close examination revealed that there was an enhancement of particle formation along imperfections within the carbon film such as folds and buckled areas creating crevices in the carbon film. Figure 5 is an example of preferential particle formation along a crevice area within the carbon film.

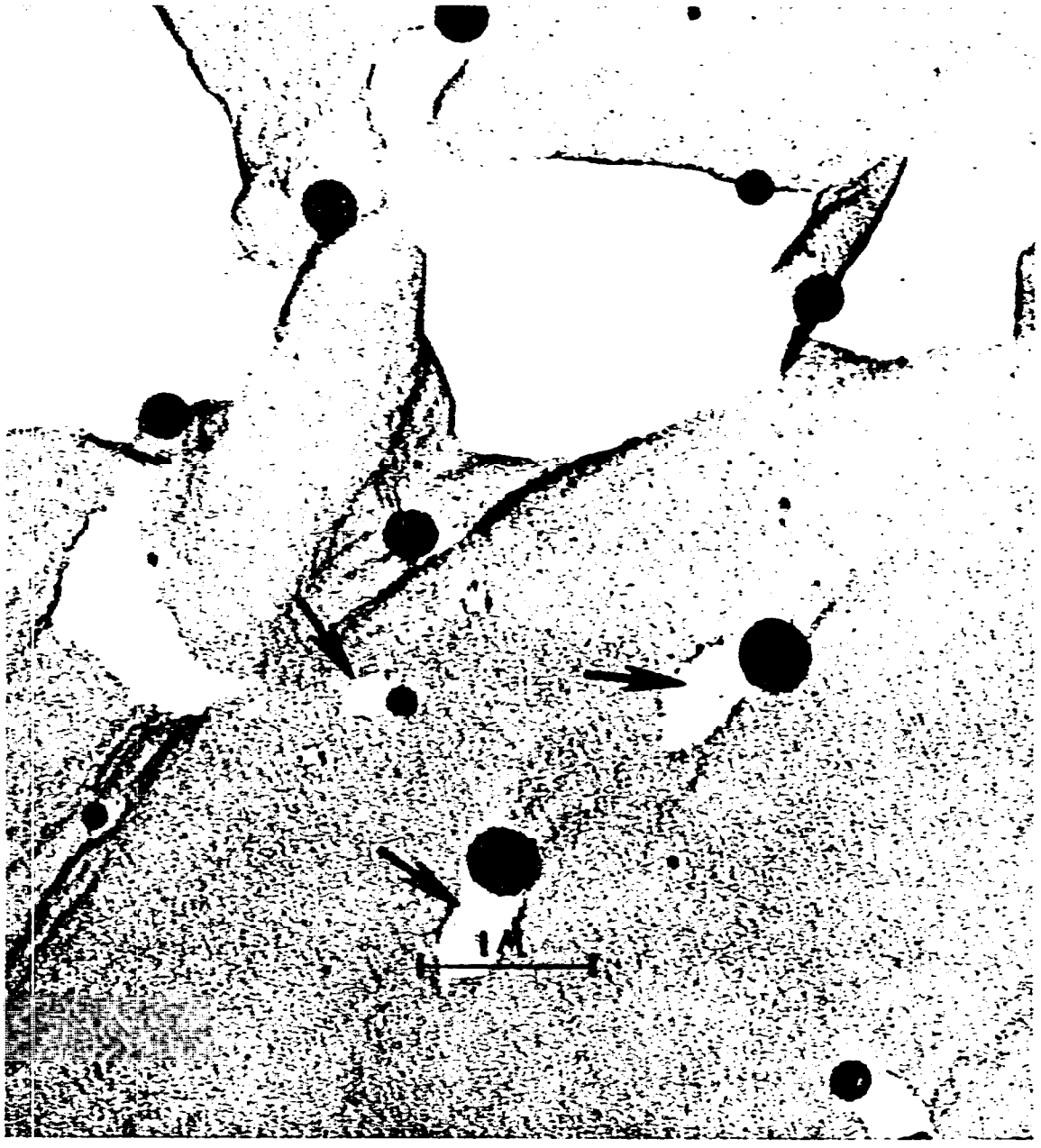

Fig. 5. Electron micrograph of particles formed on a gold grid with a carbon thin-film coating heated to 710 C for 30 minutes. Picture taken during heating cycle. Magnification, 20 400×. The arrows show areas where the carbon film has been degraded where a particle has formed.

Preferential particle formation along imperfections in the carbon film consistent with a surface migration mechanism by which metal atoms are transported from the grid bars to the carbon film. Gjostein[11] has pointed out, in fact, that where surface migration occurs the atoms would be found preferentially along such defects as those mentioned. Also, surface migration would seem to be the likely transport mechanism under the high vacuum conditions found within the electron microscope.

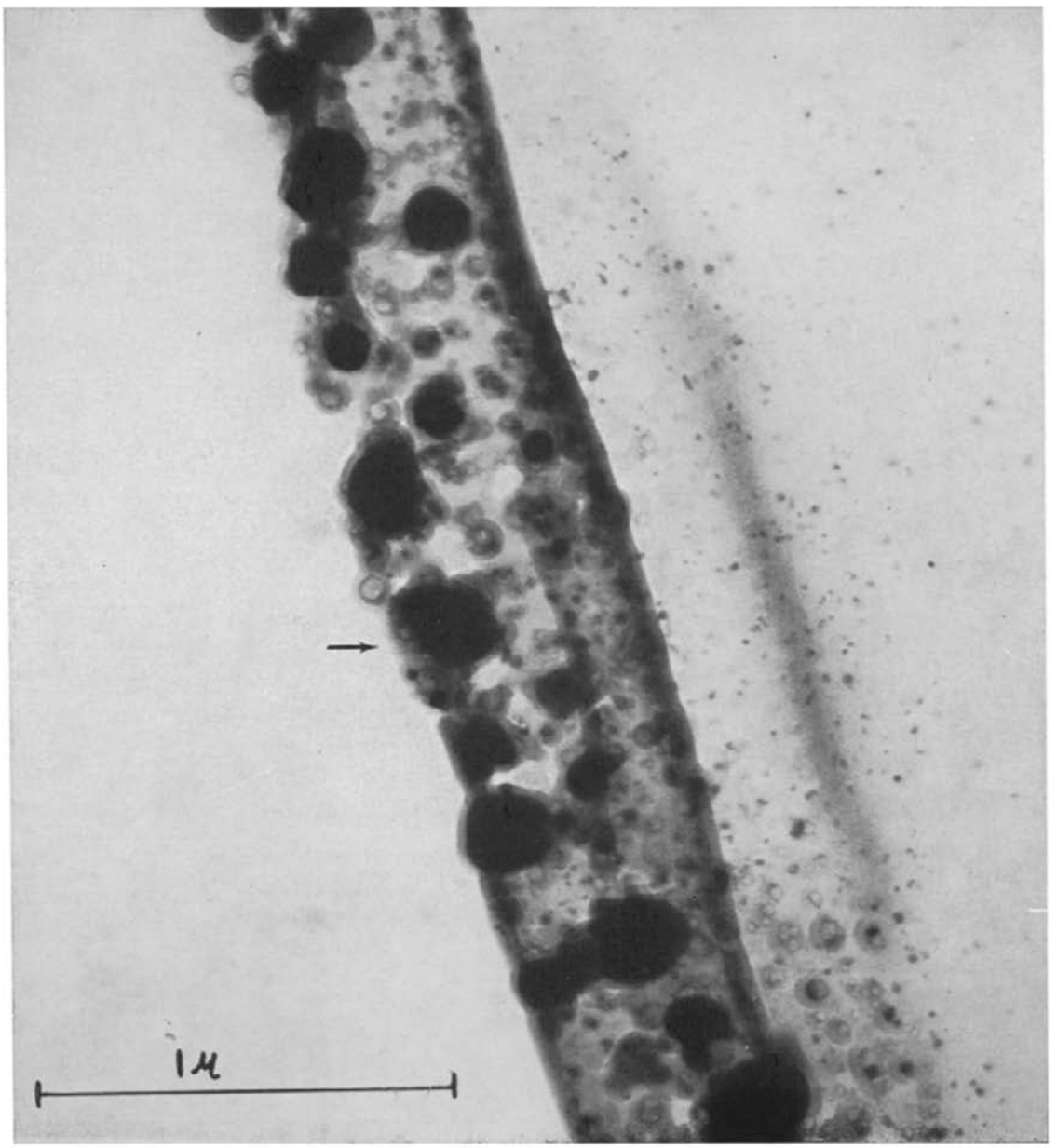

Fig. 4. Electron micrograph of particles formed on a nickel grid with a carbon thin-film coating heated to 630 C for 2 hours. Picture taken while heating. Magnification, 50 900 ×.

As was shown in the earlier work[1], the particulate matter formed on the grids was first observed at different temperatures on different types of grids. However, it was desirable to perform a study which would demonstrate conclusively that the carbon film was necessary for particle formation. Heating studies conducted using SiO coated metal grids not only served this purpose, but served to solve a problem of

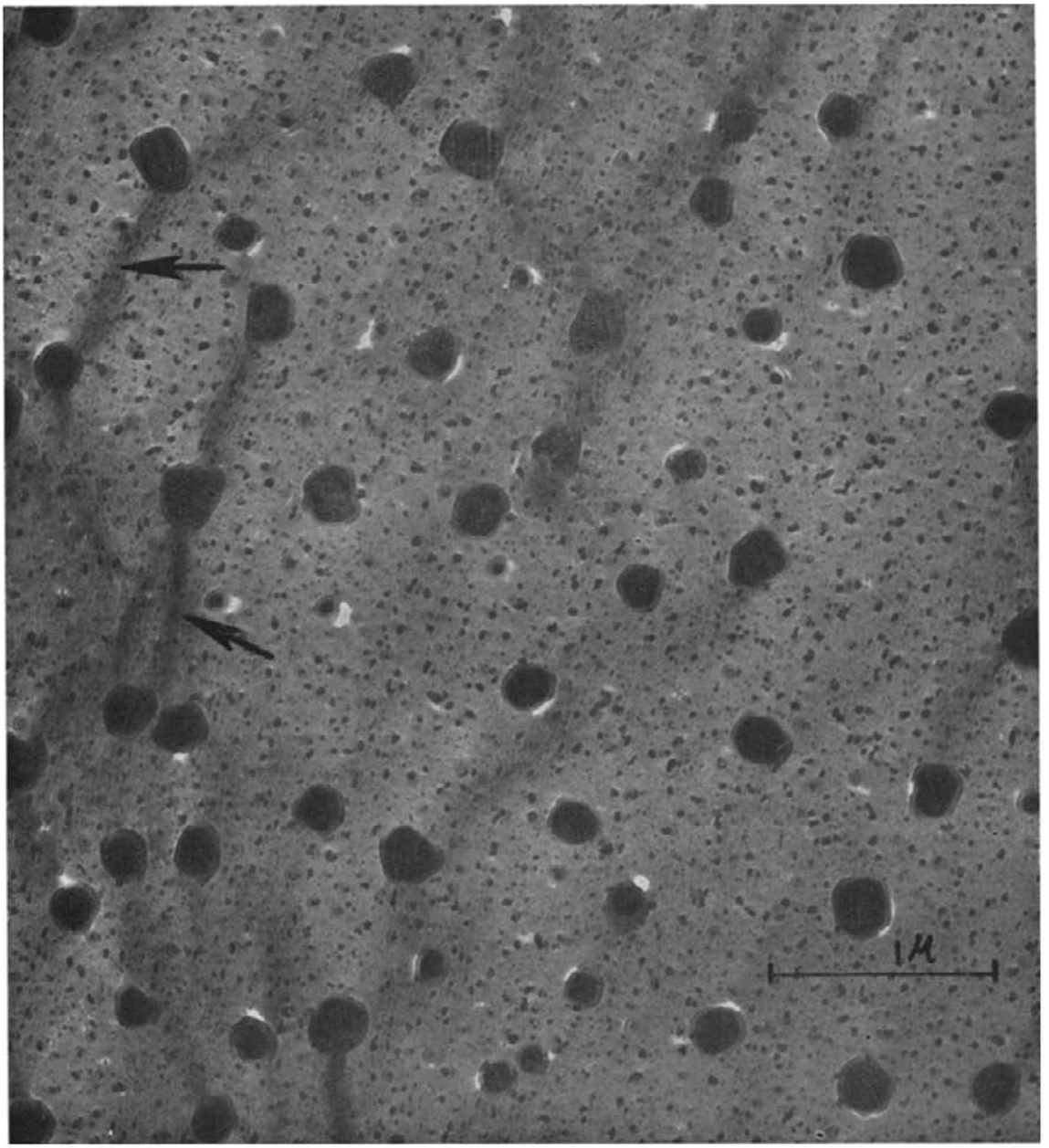

Fig. 5. Electron micrograph of particles formed on a molybdenum grid with a carbon thin-film coating heated to 700 C for 30 minutes and allowed to sit in the atmosphere for 3 months. Magnification, 26 700 ×. The arrow points to an area where the carbon film has "buckled".

MoO_2 contamination mentioned earlier[3]. When SiO coated microscope grids were heated to elevated temperatures within the microscope, only rod-shaped particulate matter was formed. Furthermore, these rod-shaped particles were formed on all types of grids at the same temperature (approximately 600 C). Determination of the d-spacings of these rod-shaped particles showed the material to be MoO_2, the

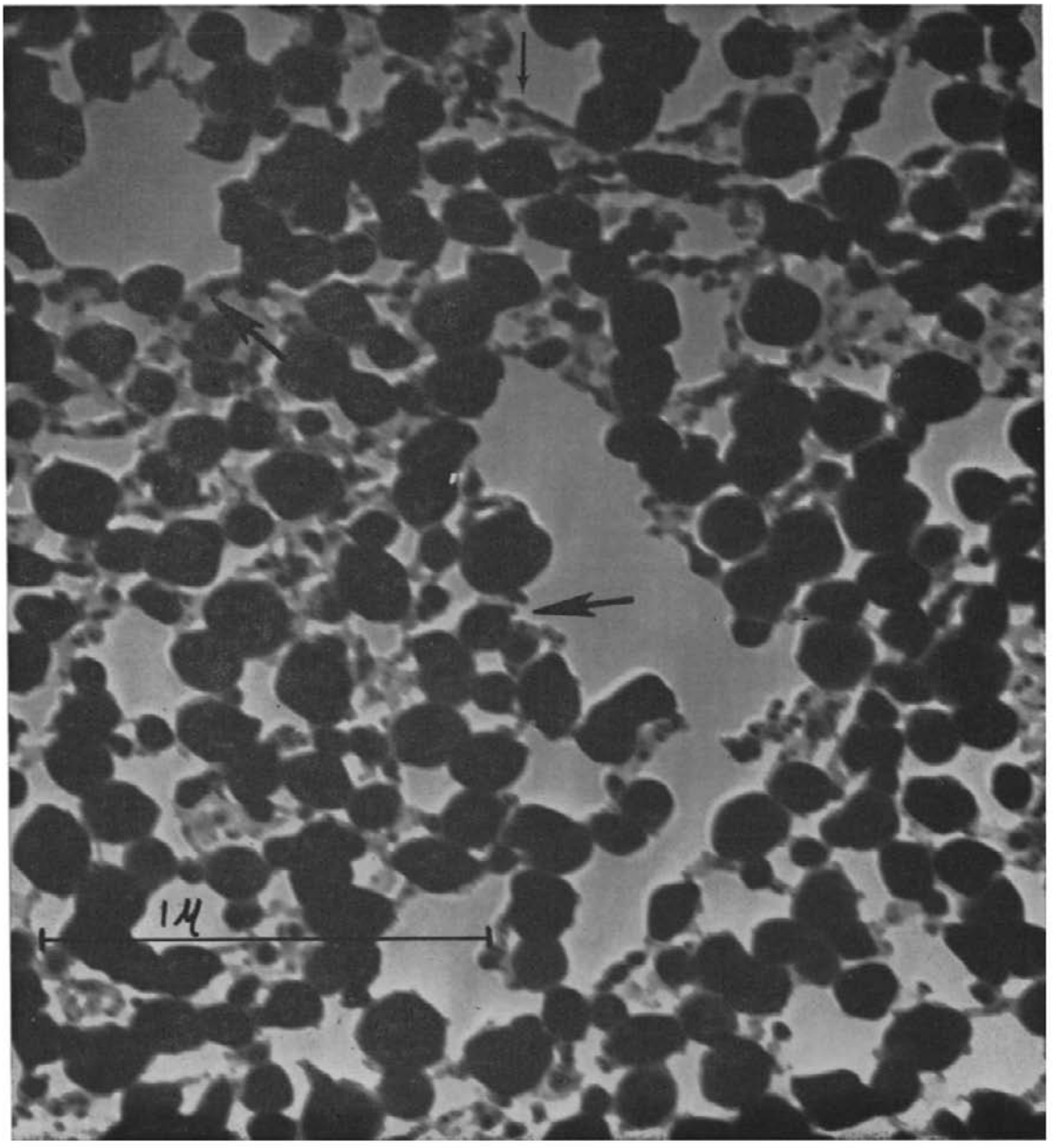

Fig. 6. Electron micrograph of particles formed on a tungsten grid with a carbon thin-film coating heated to 700 C for 30 minutes and allowed to sit in the atmosphere for 3 months. Magnification: 54 600 ×. The arrow points to an open area where the carbon film has been degraded.

source of which was shown to be the molybdenum specimen holder which had formed a thin oxide coating with repeated use. The MoO_3 contaminant was eliminated by heating the specimen holder to orange-white heat in a tungsten basket within a vacuum evaporator. When heating studies were repeated with decontaminated specimen holders, the SiO coated grids showed no alterations or particle formation

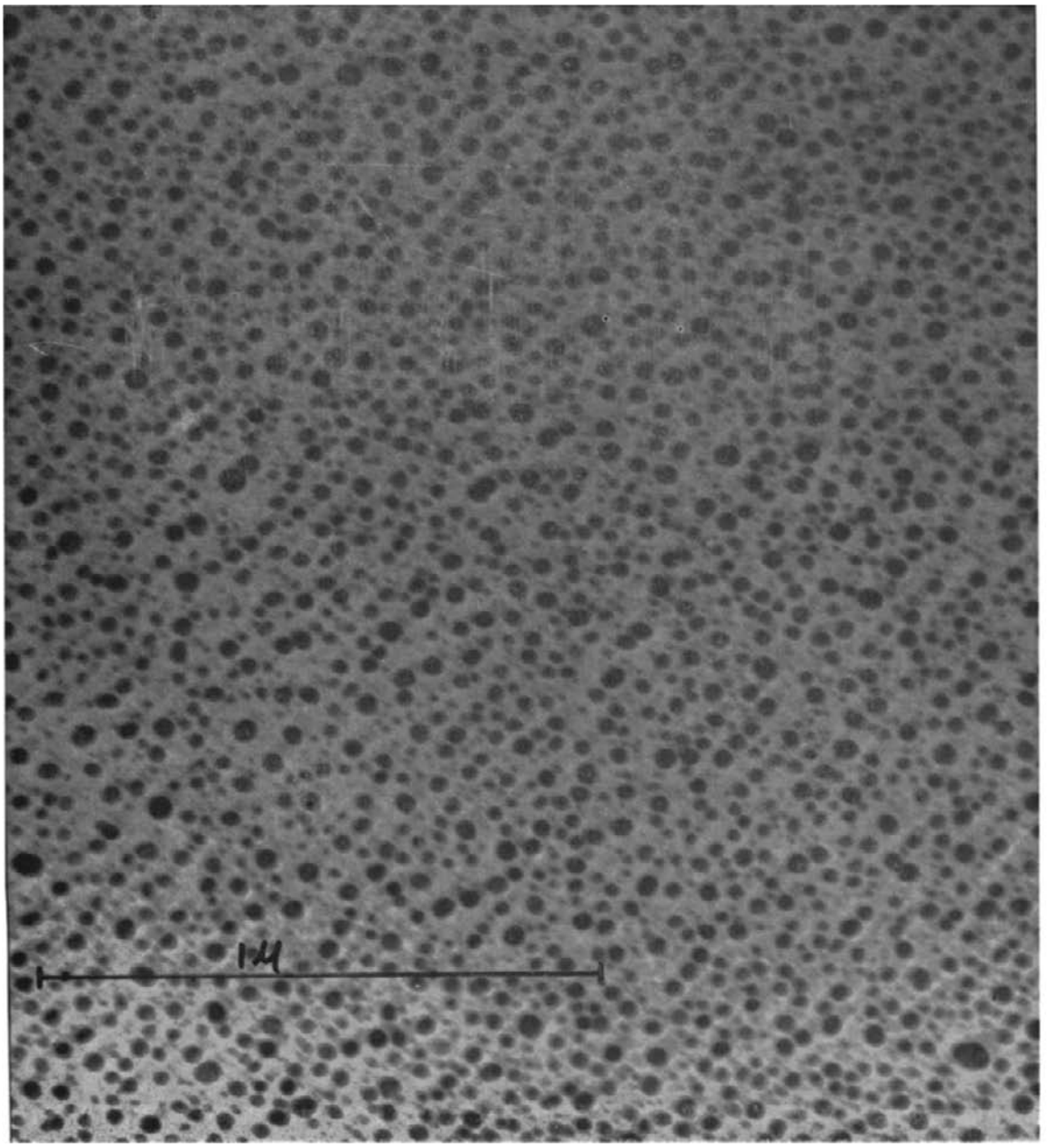

Fig. 7. Electron micrograph of particles formed on a titanium grid with a carbon thin-film coating heated to 870 C for one hour and 30 minutes. Picture taken while heating. Magnification, 68 800 ×.

from room temperature to 800 °C. On the other hand the carbon coated grids formed the angular particles shown in the figures at the temperatures given in Table 1 and gave the electron diffraction data shown in Table 2. All of the studies reported in this work were performed without the problem of MoO_2 contamination which was not true of earlier studies[1].

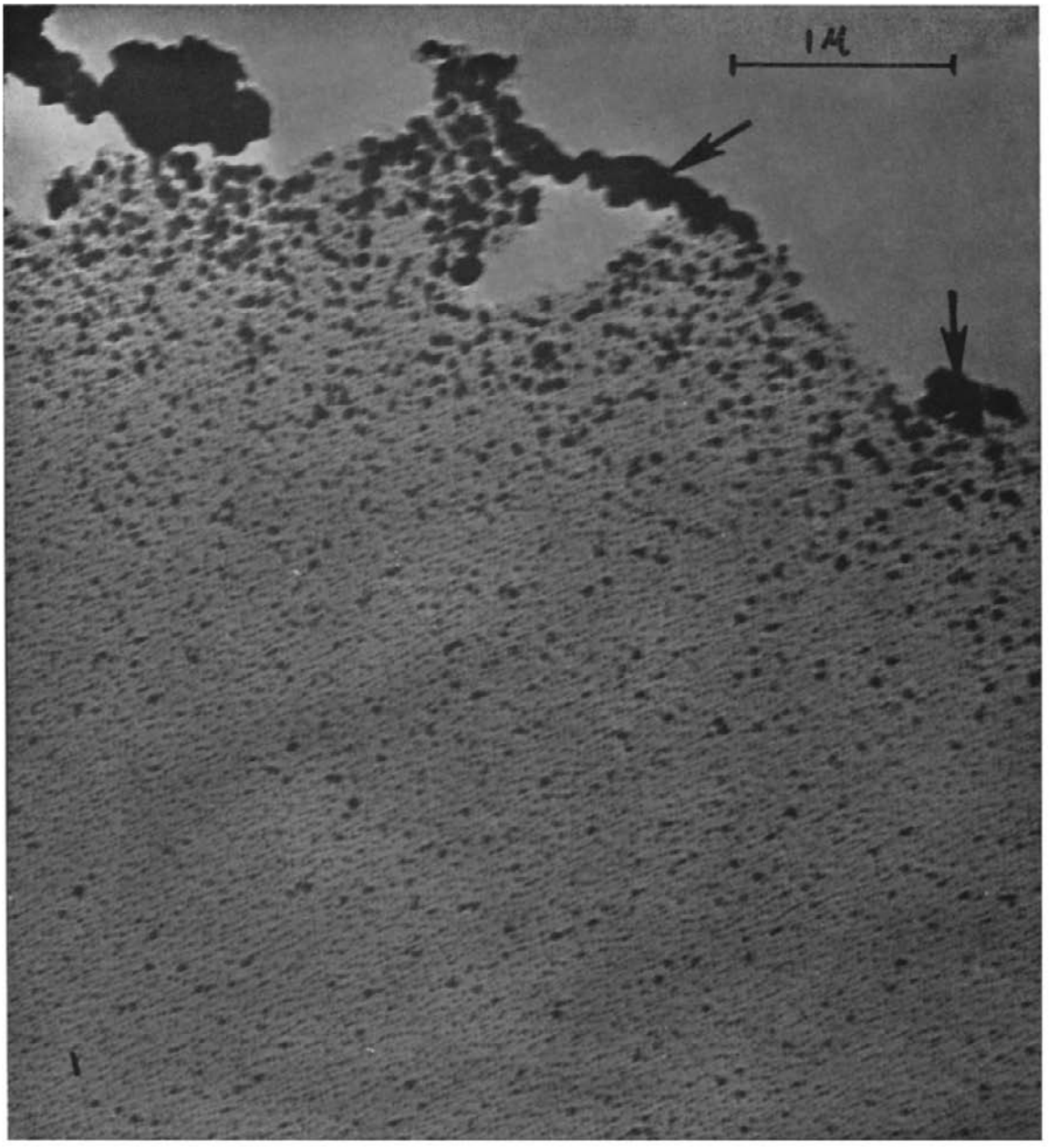

Fig. 8. Electron micrograph of particles formed on a stainless steel grid with a carbon thin-film coating heated to 850 °C for one hour and 30 minutes. Picture taken while heating. Magnification, 26 400 ×. The arrow points to the edge of the carbon film where large particles are formed.

TABLE 2

SELECTED-AREA ELECTRON DIFFRACTION DATA (d-spacings (Å)) FOR CARBON FILM COATED GRIDS HEATED TO ELEVATED TEMPERATURES UNDER CONTINUOUS HEATING

Cu	*Ni*	*W*	*Mo*	*Au*	*Ti*	*Stainless steel*	*Ag*
		6.5		6.4		6.5	
		5.1				5.0	5.2
		4.2	4.4		4.3		4.5
	3.9	3.75			3.74	3.6	
	3.38	3.26					
		3.06	3.04	3.05	3.05	3.02	3.04
	2.91	2.95	2.91	2.93		2.98	
	2.77	2.71			2.62	2.62	2.59
	2.61	2.67	2.55	2.55		2.53	
2.36	2.43	2.44	2.45	2.45			
2.11	2.14	2.05	2.24	2.34		2.39	2.43
	2.04	1.91	2.08	2.16		2.28	
1.82	1.97	1.84	1.93	2.13			2.16
	1.83	1.68	1.70	1.93			2.11
	1.77	1.62		1.68	1.76	1.75	
1.49	1.70	1.41	1.47	1.63		1.62	1.66
	1.52	1.37		1.48	1.52	1.51	1.53
1.30	1.46	1.33		1.42		1.49	1.48
1.27	1.40	1.24	1.26	1.30	1.35	1.36	
	1.34	1.17	1.20	1.22	1.28	1.27	1.26
1.10	1.29	1.12	1.14	1.14	1.15	1.22	1.21
	1.21			1.08			
	1.17			1.04			
	1.14			1.02	1.02		
	1.08		1.03				
	1.03						

TABLE 3

ELECTRON MICROPROBE ELEMENTAL ANALYSIS OF THE PARTICULATE MATTER FORMED ON THE CARBON COATED MICROSCOPE GRIDS AT ELEVATED TEMPERATURES

Types of grids	*Elements detected*	
	Major constituent	*Minor constituent*
Copper	Cu	
Silver	Ag	Cu
Gold	Au	Cu
Nickel	Ni	Cu
Molybdenum	Mo	Cu
Tungsten	W	Cu, Fe (trace)

The presence of the metallic elements within the carbide particles was demonstrated by qualitative analysis performed on individual particles by electron microprobe analysis. Because of a limited amount of available time on the scanning electron microscope, analysis was not made on stainless steel and titanium grids. The data for this analysis is presented in Table 3 and verifies the presence of the metals of the various microscope grids within the particles formed on the carbon films. A small amount of copper was also found in the particles on all grids analyzed. The source of this copper was most likely a copper sleeve of the objective pole piece which was located directly below the sample. Copper, being a relatively volatile metal, was apparently vaporized to some extent by the heating and the copper atoms were then

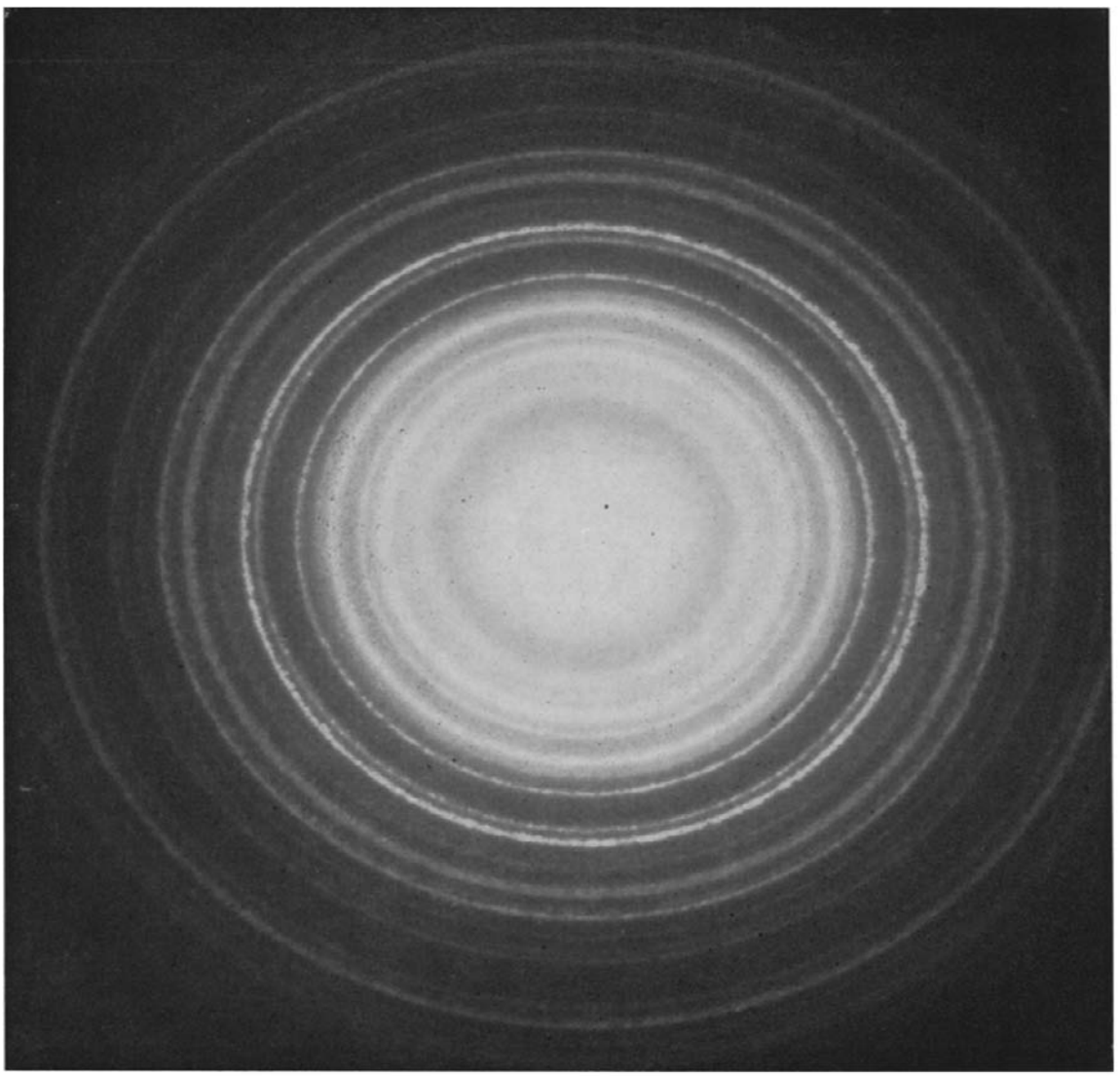

Fig. 9. Selected-area electron diffraction pattern given by particles formed on a gold grid with a thin-film coating of carbon heated to 720 C for one hour and 30 minutes. Pattern taken while heating.

drawn upward by the vacuum system where they struck the carbon film surface and became incorporated into the carbide particles. Although quantitative analysis was not made, the electron microprobe data revealed that the microscope grid metal was the major component in each case with copper being a minor component. The source of the very small trace of iron metal found in particles formed on the tungsten grid is not known, but it is possible that the tungsten metal itself may have contained iron as a trace contaminant.

In order to gain structural information about the metal carbon compounds which were observed to form, an analysis of the electron diffraction data of the various types of particles was made. The d-spacings of the various carbide particles are listed in Table 2.

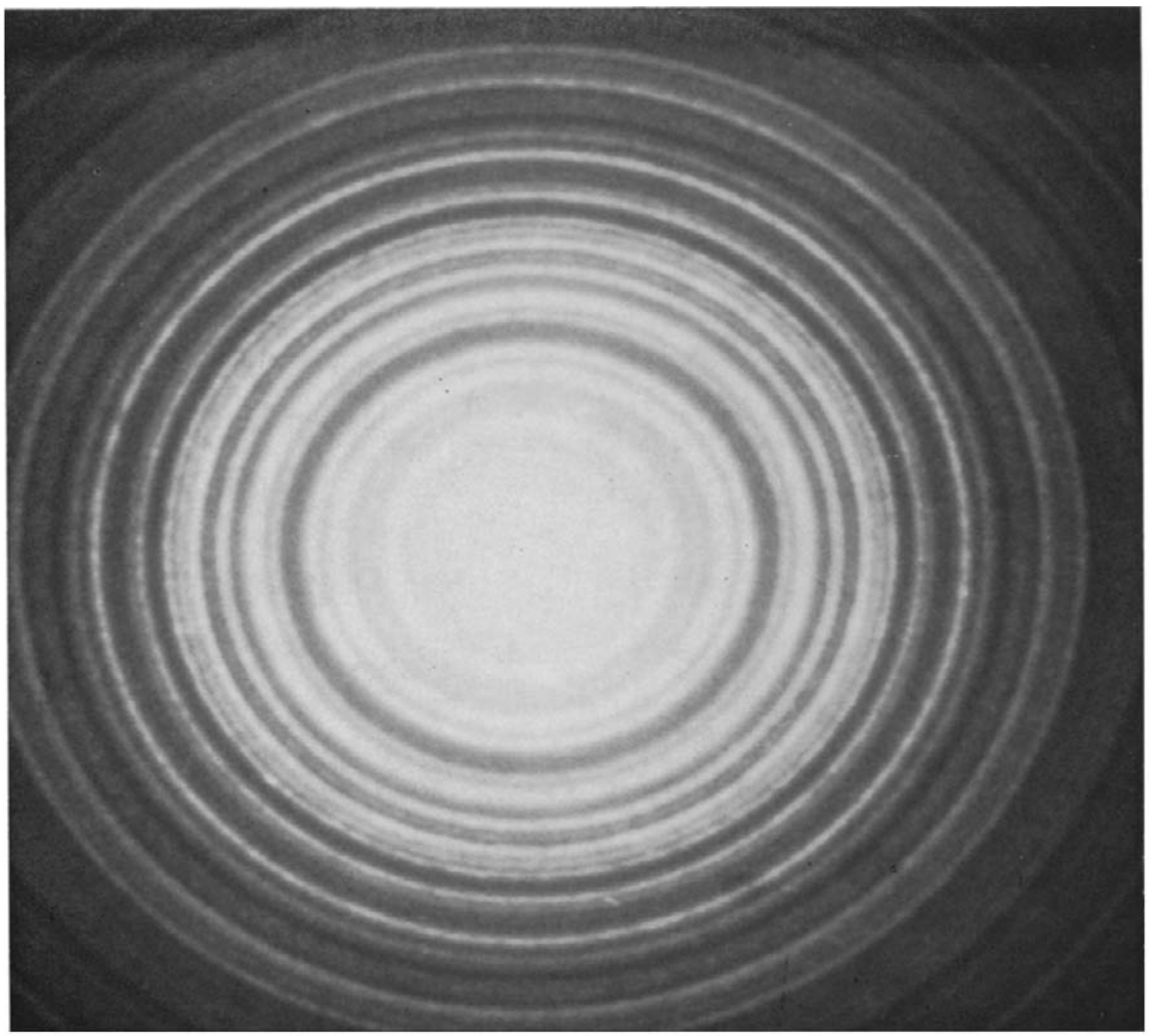

Fig. 10. Selected-area electron diffraction pattern given by particles on a nickel grid with a thin-film coating of carbon heated to 690 C for 2 hours. Pattern taken while heating.

The most important features of the electron diffraction data are: (1) the similarity in d-spacings from one type of particle to another, (2) the large number of diffraction lines observed, and (3) the presence of large d-spacings above 5.0 Å. An attempt was made to correlate the d-spacings given by the carbides formed in these studies with the d-spacings of known carbides of the same metals in order that the structural type could be identified. The three features given above completely eliminated all of the known binary carbides of the metals studied. A comparison of the d-spacings in Table 2 with those given by various ternary carbides led to the following conclusion: the carbides formed in this study gave d-spacings which were the same (within experimental error) as those given by a mixture of the complex carbides with general formulae M_6C and $M_{23}C_6$, where M represents any metal atom. Andrews[12] has called attention to the fact that these two structural types are closely related (both are face-centered cubic), and are often formed simultaneously in metal alloys at high temperatures. Andrews gave the d-spacings for an M_6C carbide with $a_0 = 11.06$ Å and an $M_{23}C_6$ carbide with $a_0 = 10.64$ Å. The X-ray diffraction data for all other known carbides are unsatisfactory in explaining the electron diffraction data, and therefore, the M_6C and $M_{23}C_6$ structural types best represent the structures of the carbides formed on the carbon films.

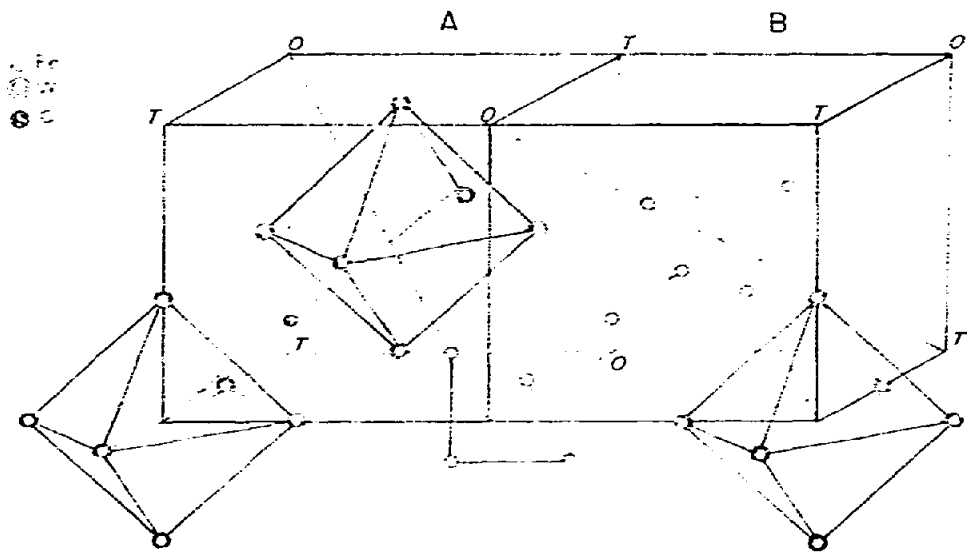

Fig. 11. Carbon environment in Fe_3W_3C and $(Cr,Fe,W)_{23}C_6$ according to Goldschmidt[7].

The structure of the M_6C carbides was first studied by Westgren[13] for Fe_3W_3C. This carbide is face-centered-cubic ($a_0 = 11.06$ Å; space group O_h^7) and contains 96 metal atoms and 16 carbon atoms in a unit cell. A portion of the unit cell is shown in Fig. 11. Westgren[14] also was the first to report the structure of the $M_{23}C_6$ type of carbides as demonstrated by $Cr_{23}C_6$ which has a unit cell length of 10.64 Å (face-centered cubic; space group O_h^5). This carbide contains 92 metal atoms and 24 carbon

atoms in the unit cell. Figure 12 shows some of the details of the unit cell for an $M_{23}C_6$ carbide according to Goldschmidt[7].

BONDING CONSIDERATIONS

The bonding in transition metal carbides is a detailed subject, and a number[6,15–18] of appropriate works can be consulted. Although an exhaustive treatment cannot be given here, the significance of the results will be given in terms of previous theories of carbide bonding. Rundle[15] and Engel[17] presented initial theories of bonding applied primarily to the simple refractory carbides such as TiC and VC. In both cases, their attention was focused on the metal–carbon bonding interaction. Engel[17] suggested that there was appreciable ionic character in the metal to carbon bonds of the refractory carbides with electron transfer from the carbon species to the unfilled d-orbitals of the metal species. Copper, silver, and gold being d^{10} systems could not participate in this type of electron transfer, and therefore, these metals would not form stable binary carbides. Rundle's[15] theory of bonding in the binary carbides such as VC and TiC regarded the metal–carbon bonds as being covalent. Rundle suggested that one of the more crucial requirements for the metal species was thatit possesses unfilled d-orbitals again excluding the possibility that copper, silver,

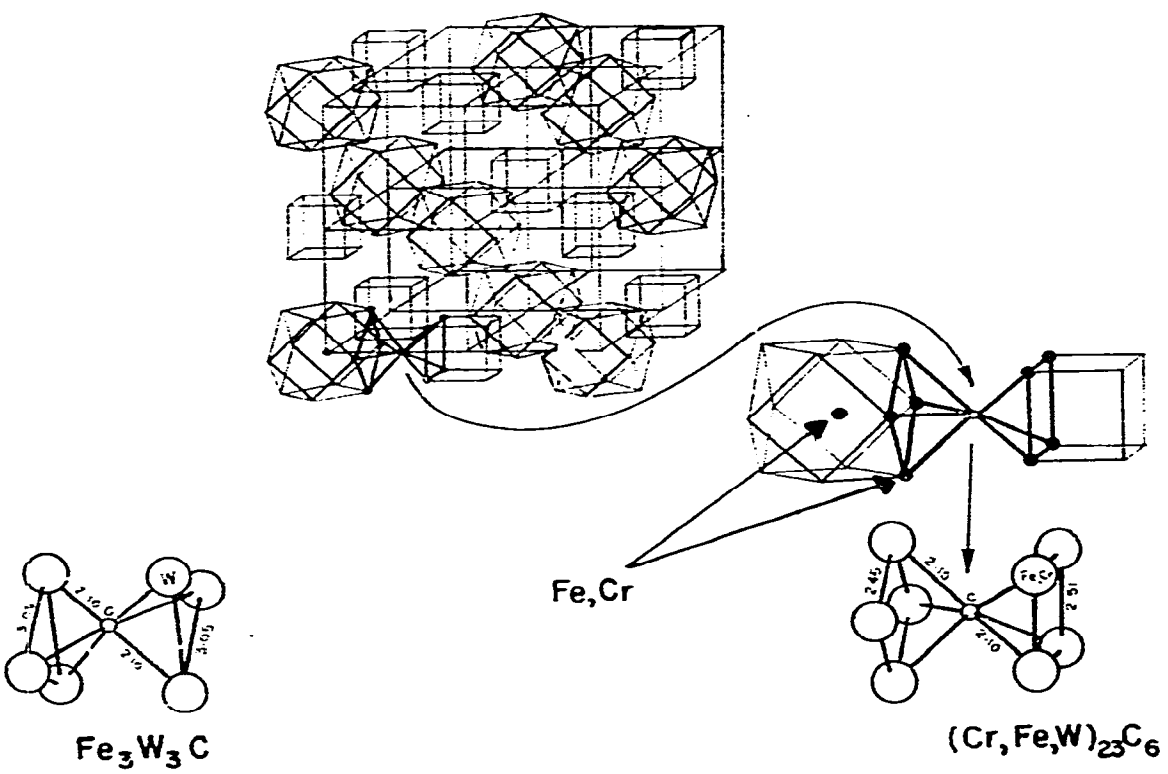

Fig. 12. Structure of Fe_3W_3C according to Westgren[14].

and gold might form stable carbides, or at least any related to VC, HfC, and TiC in structure to which these ideas of bonding were primarily directed.

The results of this study showed that copper, silver, and gold did form carbides, although those formed had a more complex structure than the simple refractory binary carbides. With the structure of the M_6C and $M_{23}C_6$ carbides in mind, it is evident that the conclusions made by Rundle and Engel for the simple binary carbides may not apply here. An examination of Figs. 11 and 12 shows that in the M_6C and $M_{23}C_6$ carbides there are more metal–metal bonds than metal–carbon bonds. The possibility of favorable metal–metal interaction in the M_6C and $M_{23}C_6$ type of carbides containing copper, silver, or gold as the metal species may serve to explain why these structural types of carbides were formed over less complex ones.

These studies have shown that carbides of copper, silver, and gold do form, along with the carbides of nickel, molybdenum, tungsten, titanium and elements of stainless steel. In addition, the carbides studied were formed at significantly lower temperatures than commonly found in other studies made primarily in the steel industry. These observations may therefore have significance when considering the chemistry of copper, silver, and gold alloys containing small amounts of carbon.

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