

## Carbon Formation on Copper-Nickel Alloys from Benzene

Y. NISHIYAMA AND Y. TAMAI

*Chemical Research Institute of Non-Aqueous Solutions, Tohoku University,  
Sendai, Japan*

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Carbon formation by the decomposition of benzene on copper-nickel alloy sheets and powders was studied in a temperature range from 580 to 900°C. Two types of carbon were observed: one (type A) formed at higher temperatures was a flat thin film and the other (type B) formed at lower temperatures was a black powder. The rate of type A formation was small and nickel-rich substrates catalyzed it only at the initial stage. The rate of type B formation was considerably large and the alloys of 80 to 40% nickel had stronger catalytic activity than pure nickel. In this carbon, large amounts of metal particles were present in the same composition as that of substrates. A possible mechanism for the deposition is discussed.

### INTRODUCTION

The formation of a carbonaceous solid over metal surfaces by the decomposition of carbon-containing gases has been the subject of numerous studies. It is well known that iron, cobalt, and nickel are active catalysts for carbon formation while copper and platinum are, in most circumstances, inactive (1-10). It is also known that these catalytic metals are found in the carbon body separated from the substrates (1-4, 9-14). Several forms of carbon deposit have been reported, e.g., flaky, feather-like, and amorphous. Among them is a fibrous carbon, frequently with metallic particles at the ends or halfway (1, 2, 4, 9, 12-15). These observations awaited an explanation with which the mechanism of metal transportation as well as the durable catalytic activity even after the formation of macroscopic carbon layer over metal surfaces could be understood. Baird *et al.* suggested the incorporation of atomically dispersed metal in the carbon layer (12). Recently, Lobo *et al.* (7, 22) reported that there are three kinetic regions of carbon formation from olefins on nickel depending on the temperature, and proposed a mechanism in which carbon atoms produced at the surface migrate to the active sites or grain boundaries and form a carbon deposit.

In the course of a study in this laboratory on the homogeneous decomposition of hydrocarbons in metal reactor, copper-nickel alloys of a particular composition range were observed to have stronger catalytic activity for carbon formation than pure nickel (16). Thus the present investigation was undertaken to correlate the nature of metal surface with the catalytic activity for carbon formation.

The results seem to suggest a mechanism similar to that of Lobo *et al.* Besides, the present study provides an interesting case of relation of catalytic activity with the composition of alloys that varies when the mechanism of the reaction changes.

### EXPERIMENTAL

#### *Apparatus*

Carbon was deposited either on a sheet or a powder of metal placed in a quartz reactor by passing a stream of benzene vapor through which was carried by a helium flow. The amount of deposition was measured by the weight increases of the specimen. A quartz spring balance was used to follow the weight changes continuously, and measurements by microbalance after deposition runs were employed to compare the

total amounts of deposition between different specimens set at the same time.

The reactor, a quartz tube of 2.6 cm i.d., was heated by an electric furnace and had a rectangular temperature profile along its axis with a plateau of 12.5 cm, except for runs in a temperature gradient. The temperature was kept constant within  $\pm 5^\circ\text{C}$ . The specimens were placed at the downstream end of the plateau in a tungsten holder, except for spring balance measurement when they were located around the center of the heated zone.

### Materials

The sheets of alloys were obtained by cold rolling alloy rods to 0.01-cm thickness and were cut into 1.0-cm square. They were polished with fine alumina powder and washed carefully with a detergent and, then, distilled water. The original rods had impurity contents of 0.4% or less. Nickel specimen of 99.7% purity will be referred to as 100% nickel or pure nickel for convenience.

The powder samples in a form of oxide were prepared by the coprecipitation from mixed nitrate solutions by ammonium bicarbonate and subsequent calcination, in accordance with the manner described by Sinfelt *et al.* (17). The oxide powders between 0.03 and 0.06 cm were sifted and were used for deposition runs.

A guaranteed reagent grade benzene was used without further purification as carbon source. Helium was passed through columns packed with activated copper at  $170^\circ\text{C}$  and molecular sieve 4A at room temperature. Hydrogen was passed over palladium catalyst at  $250^\circ\text{C}$  and then molecular sieve 4A column.

### Procedures

In the reactor, the sheet specimens were first treated with hydrogen at atmospheric pressure and at the reaction temperature for 15 min. The hydrogen was then evacuated and the reactor quickly filled with benzene-containing helium, before a constant helium flow was established. The partial pressure of benzene was kept at 8000 N

$\text{m}^{-2}$  by maintaining the temperature of the evaporator at  $15.4^\circ\text{C}$  throughout the present experiments. Unless noted otherwise, the flow rate of helium was  $12.5 \pm 0.5 \text{ cm}^3$  (STP)/min, which carried 3.5 mg/min of benzene. The average residence time of benzene in the heated zone varied from 76 s (at  $900^\circ\text{C}$ ) to 100 s ( $600^\circ\text{C}$ ). Though the flow rate of the reactant was seen to have some influence on the deposition rate, those experiments in which flow rate was kept constant will be reported here to put emphasis on comparison of activity of different substrates.

In the case of powder specimens, oxide powder was mounted on a quartz pan, set in the reactor, heated in a stream of hydrogen at  $680^\circ\text{C}$  for 120 min, and, after evacuation, a carbon deposition run was conducted.

### X-Ray Analysis

An X-ray instrument, Shimadzu VDF-2, was used for diffraction analysis using  $\text{Cu-K}\alpha$  radiation and for X-ray fluorescence analysis. Quantitative analysis of the copper-nickel alloy in carbon was performed using mixtures of copper- and nickel-dimethyl glyoxime as standard.

## RESULTS

### General Feature of Carbon Formation

The temperature dependence of deposition was first studied qualitatively in the following manner. The furnace was set to have a smooth convex temperature profile along the reactor axis with a maximum at the center, covering a range from 400 to  $910^\circ\text{C}$ . Long strips of metal substrates, each  $20 \times 0.5 \times 0.01 \text{ cm}^3$ , were placed in the reactor and benzene vapor was passed over them for 60 min.

The appearances of the strips after deposition showed a clear distinction between two types of carbon; a thin lustrous film, referred to as type A, at the central region of the strips and an aggregate of carbon particles like carbon black, referred to as type B, on both sides of the strips at some lower temperature zones. The temperature ranges within which these carbon appeared

TABLE 1  
TEMPERATURE RANGES IN WHICH VISIBLE  
DEPOSITION OCCURRED<sup>a</sup>

Substrate (% Ni)	Type A <sup>b</sup>	Type B <sup>b</sup>	
		Inlet side	Outlet side
100	>860	Obscure	660-795
80	>855	710-810	630-810
60	>860	710-825	640-780
40	>855	730-825	660-810
20	Obscure	780-845	Obscure

<sup>a</sup> Temperature in °C.

<sup>b</sup> See text for definition.

are given in Table 1. The transient regions between them retained the metallic appearances of the substrates.

#### Rate of Type A Carbon Formation on Sheet

The weight increases of the sheets by carbon deposition at 890°C were rather small to follow continuously, so several specimens of the same composition were treated for different durations. The results are shown in Fig. 1. As seen, the rate of deposition is almost constant except the initial short period in which rapid deposition occurred on nickel-rich substrates. Thus, for type A, the metals exert a catalytic effect only at the very initial stage of deposition and the growth of the carbon layer seems to be noncatalytic.

#### Rate of Type B Carbon Formation on Sheet

The rate of type B deposition was measured at 580, 680 and 770°C. Typical re-

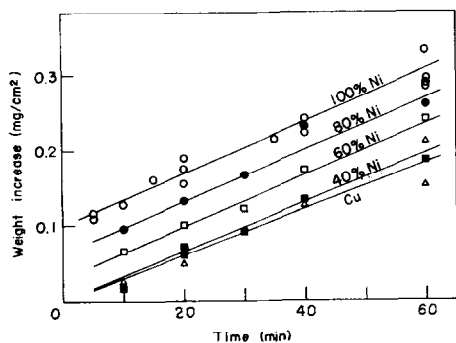


FIG. 1. Carbon deposition on copper-nickel alloy sheets at 890°C. (○) 100% Ni, (●) 80% Ni, (□) 60% Ni, (■) 40% Ni, (△) Cu.

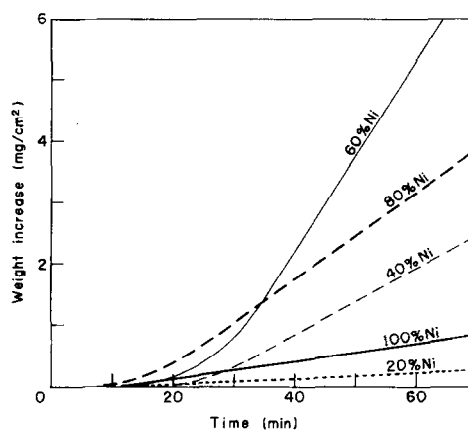


FIG. 2. Carbon deposition on copper-nickel alloy sheets at 680°C.

sults obtained by spring balance at 680°C are shown in Fig. 2. There is an induction period of about 20 min and after this, the rate is practically constant for each substrate. The amounts of deposition after 60 min of reaction, compared in Fig. 3, are not so reproducible but clearly indicate that alloys of 80 to 40% nickel are far more active than pure nickel and that type B depo-

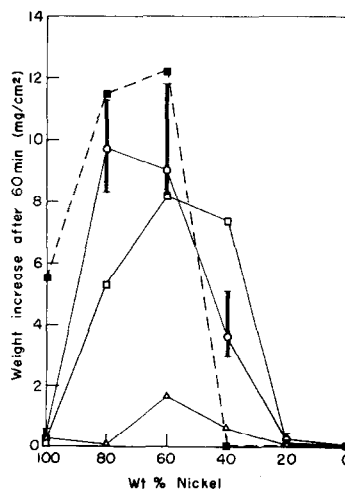


FIG. 3. Comparison of the amounts of deposition after 60 min. (△) 580°C, (○) 680°C, (□) 770°C, (■) 770°C in hydrogen carrier. Each plot represents the median of four to seven measurements, except for those in hydrogen (once for each). The vertical strips attached to the plots for 680°C show the magnitude of scattering of individual measurements.

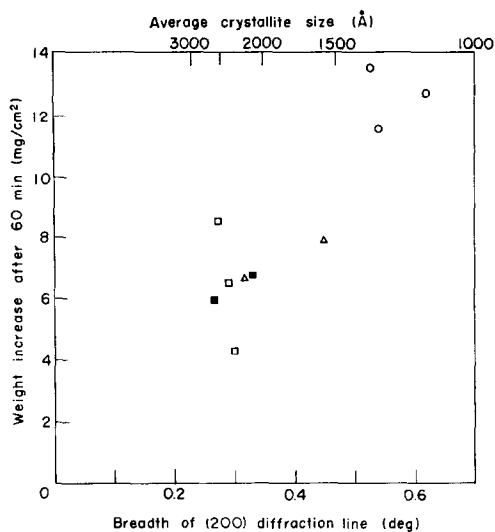


FIG. 4. Effect of heat treatment of the sheets of 80% nickel on the carbon formation at 680°C. (○) 680°C, 15 min, (△) 770°C, 60 min, (□) 890°C, 60 min, (■) 920°C, 105 min. The X-ray diffraction was measured before the deposition run.

sition on these metals is about forty times faster than type A.

A few specimens of 80 and 60% nickel were heated at 770 or 900°C in helium prior to the deposition run at 680°C. This treatment reduced the amount of deposition by 20 to 50%, though the deposits were still of type B. In a few cases, heat-treated specimens of 80% nickel were examined by X-ray diffraction before and after the

deposition runs. In Fig. 4, the weight increases of these are plotted against the pure breadth of (200) diffraction line before deposition. It is seen that the amount of deposition decreases when the average crystal size increases. Considerable decrease of the crystal size was found after a severe deposition occurred.

#### Carbon Formation on Powder

The deposition runs on powder specimens were conducted at 680°C with a reduced flow rate of helium,  $6.5 \pm 0.5 \text{ cm}^3$  (STP)/min, which carried benzene vapor at a rate of 1.8 mg/min. The results are given in Fig. 5.

The rate of deposition on nickel-rich powders (100 and 85% Ni) decreased markedly after they were coated with some amounts of carbon, which were roughly proportional to the total amount of metals. A rough estimate using the macroscopic diameter of the powder gave about 200 mg/cm<sup>2</sup> for the coverage on 85% nickel when the rate became slow. Most strong activity was found on 70 and 55% nickel when the rates of deposition were restricted by the rate of benzene supply. The deposition on 40% nickel had a rather long induction period after which the rate increased progressively. On 20% nickel, the deposition was very slow and the appearance of powder after 300 min of reaction was not uniform; some of the metal particles were

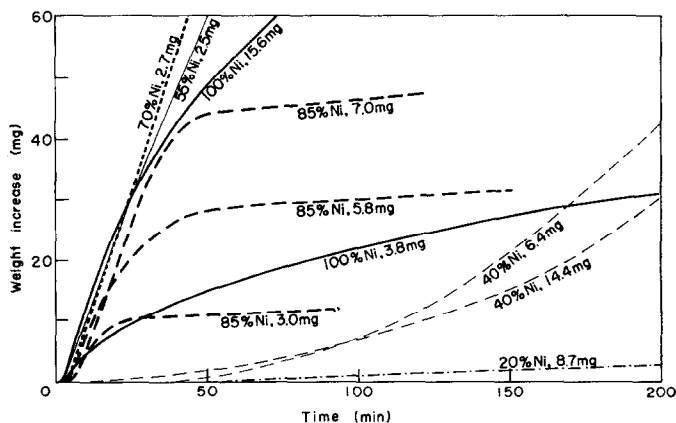


FIG. 5. Carbon deposition on alloy powders at 680°C. The weights marked in the figure are those of powders after reduction.

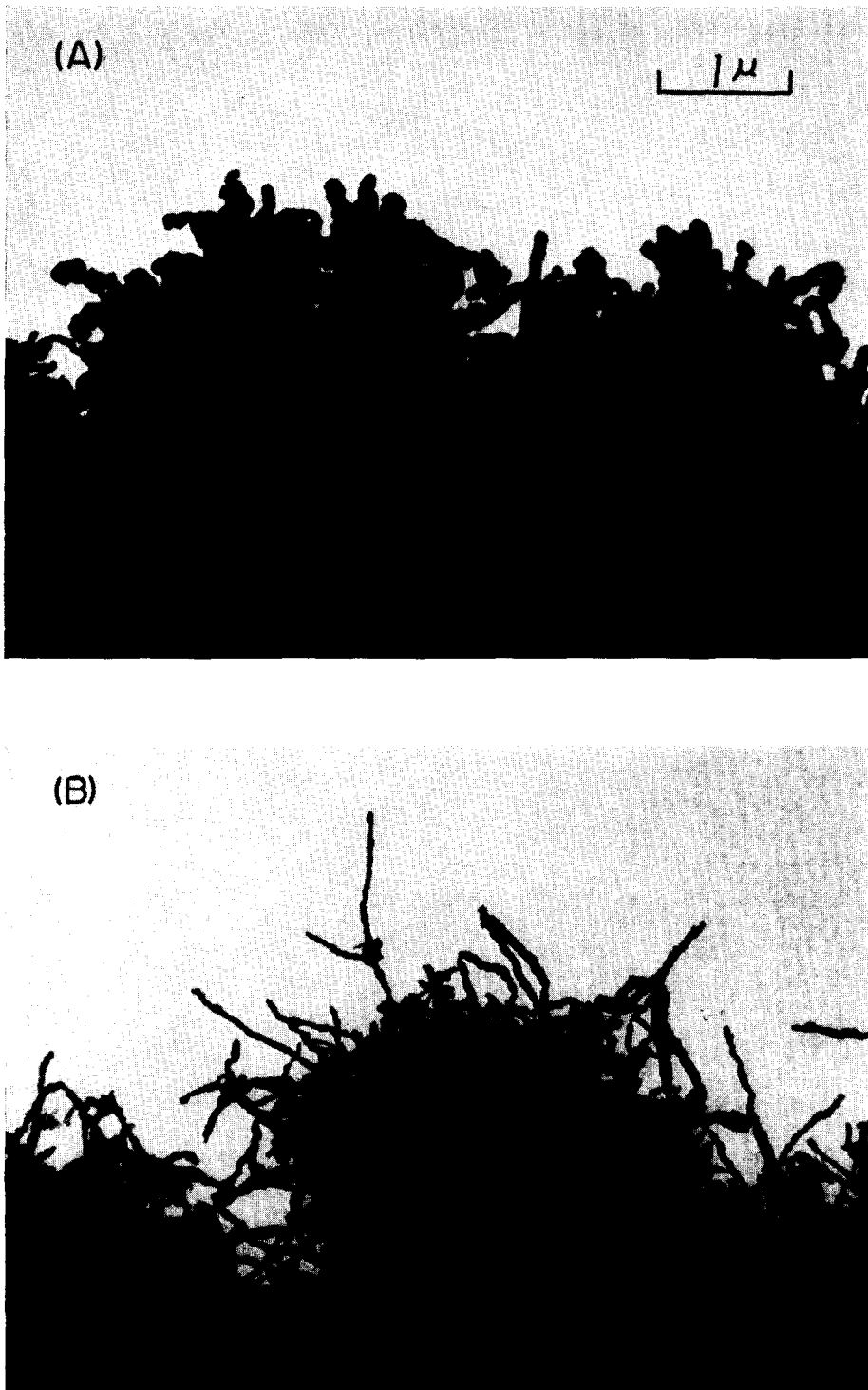


FIG. 6. Electron microscope photographs of type B carbon deposited at the edges of metal sheets. (A) On 100% Ni at 680°C after 20 min of reaction; (B) 80% Ni, 680°C, 5 min; (C) 60% Ni, 680°C, 5 min; (D) 40% Ni, 680°C, 20 min.

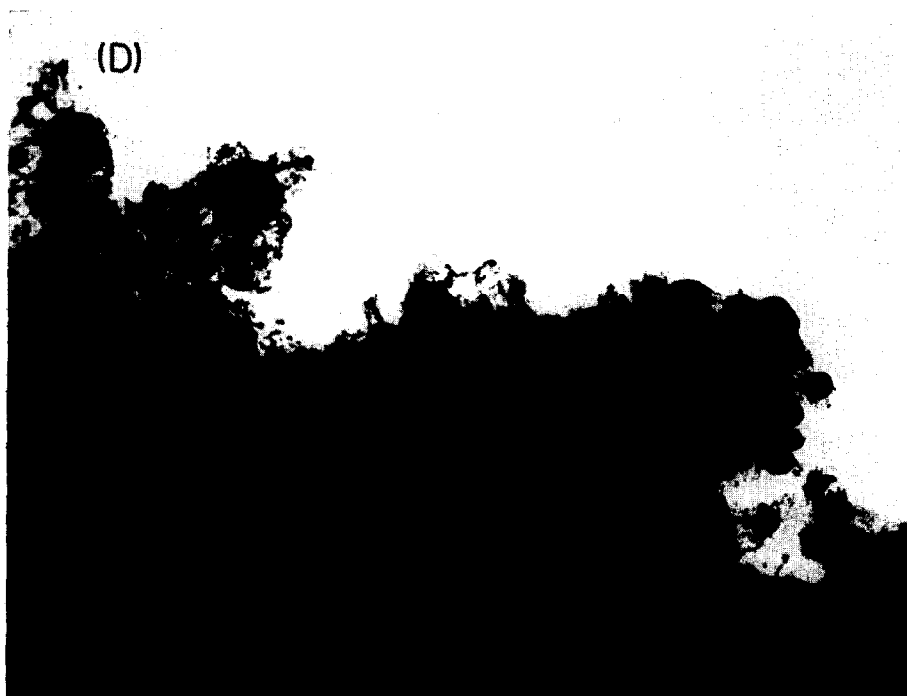
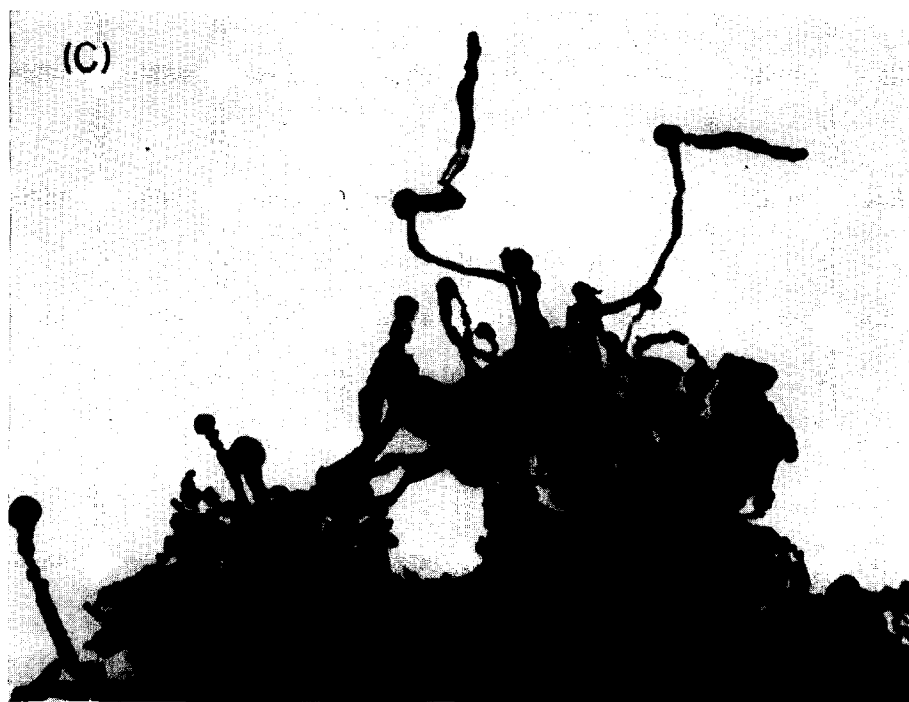


FIGURE 6C and D.

coated with carbon, while the majority retained their metallic color. The initial amounts of powders had no relation to the deposition rate for the cases of 70 and 55% nickel as well as of 40% nickel.

In addition to the above, a deposition run on 85% nickel was conducted at 885°C. Only 1.3 mg of carbon was formed onto 8.7 mg of powder after 75 min.

### Effect of Hydrogen

The effect of the presence of hydrogen in the deposition atmosphere was studied by using hydrogen as carrier. The results at 770°C are included in Fig. 3. All the experiments on the effect of hydrogen, including type A and B deposition on sheets and type B on powders, showed the same trend; i.e., hydrogen markedly accelerated carbon formation on pure nickel or nickel-rich substrates and inhibited deposition on copper or copper-rich substrates. At 890°C, hydrogen doubled the deposition on nickel after 60 min and suppressed that on copper completely.

### Analysis of the Deposits

The content and the composition of metals in the carbon layer which could be easily separated from the sheet substrates were analyzed by X-ray fluorescence and diffraction methods. The main results for type B carbon, tabulated in Table 2, are from three to five examinations for each kind of metal. Though X-ray fluorescence was rather poor in quantitative analysis, it shows that the deposit contains 4 to 27% of metal in substantially the same com-

position as the original when the amount of deposit is 3 to 12 mg/cm<sup>2</sup>. Type A carbon formed at 890°C had a very small amount of nickel (less than 0.5%) but no positive evidence of the presence of copper. The size of metal crystallite was calculated from the angular width of diffraction peaks using Scherrer's equation. It could be said that the size of the metal crystallite was not so much reduced when they were introduced into the carbon layer. Also, diffraction patterns of metal particles found in carbon did not show any sign of phase separation.

Figure 6 shows electron microscope observations of type B carbon grown at the edges of the sheets. The details of this procedure will be reported later. The fibrous nature of carbon, at least at the initial stage, and the presence of large particles (perhaps metals) at the ends are clearly demonstrated. It is interesting to note that the ratio of particle diameter to that of the fiber is larger for the fibers formed on metals of higher copper content.

The nature of type B carbon with metal particles was characterized by a few methods. The surface area, determined by argon adsorption at -196°C, was 100 m<sup>2</sup>/g. The (002) spacing by X-ray diffraction was 3.364 Å, which corresponded to a degree of graphitization, defined by Maire and Méring (18), of about 88%. Average crystallite size from the width of diffraction peak was 130 to 180 Å. From these features, type B carbon can be classified as a kind of highly graphitized carbon black.

Type A carbon may be of the same type

TABLE 2  
ANALYSIS OF METALS IN THE CARBON DEPOSITS FORMED AT 680°C

Substrate (% Ni)	Amount of deposition (mg/cm <sup>2</sup> )	Metal content <sup>a</sup> (wt%)	Ni fraction <sup>b</sup> (wt%)	Average crystal size (Å)	
				In carbon	Substrate <sup>c</sup>
80	8.3-11.7	3.7-5.1	80-82	920	1300
60	8.4-11.8	8.1-8.8	57-65	1200	950
40	3.0-5.2	19.6-27.0	38-44	260	370
20		Tr			1400

<sup>a</sup> 100(Cu + Ni)/(C + Cu + Ni).

<sup>b</sup> 100 Ni/(Cu + Ni).

<sup>c</sup> Substrate before deposition run, heated in H<sub>2</sub> at 680°C.

as the graphite films reported by Karu and Beer (19) and others (9, 20).

## DISCUSSIONS

### *Mechanism of Type A Carbon Formation*

For type A deposition, the substrates of higher nickel content showed some catalytic activity only at the very initial stage. It may be worth noting that the activity seems to decrease as the d-band vacancies are filled and to vanish at 40% nickel. A similar pattern is reported for hydrogenation of benzene in connection with Dowden's theory (21). Thus, this initial stage might be controlled by the rate of chemisorption of benzene on the metal surface. Further growth takes place on the graphite surface by condensation of benzene or active species formed in the gas phase and nickel atoms could be incorporated into the film as suggested by Baird *et al.* (12), but these have a negligible effect on further chemisorption or benzene decomposition.

### *Mechanism of Type B Carbon Formation*

Type B carbon grows undoubtedly by the catalytic action of metals and the active sites on the surface are not covered by the products, i.e., metals, whether they are in a form of reduced metal or of carbide, are brought to the surface of the layer of the deposit and keep their activity. The observations in the literature (4, 6, 22) as well as in the present study indicate that metals are carried as particles not as separate atoms. The following deposition mechanism would be a feasible one to account for the experimental results. The reactant, benzene, decomposes on the metal surface by its catalytic action and leaves carbon residues. These diffuse into the bulk of the metal, either by dissolving in the metal or by diffusion through the surface and grain boundaries, and aggregate at some active sites along grain boundaries to form carbon nuclei. These nuclei grow to macroscopic carbon through the eventual supply of carbon atoms and push the metal grains out of the substrate.

Preferential nucleation at grain boundaries is assumed because the interfacial

energy between carbon embryo and metal would stabilize the smaller embryo and lead to a higher rate of nucleation than that on the outer surface, if the rate of diffusion is sufficiently large. However, we would not exclude the possibility of nucleation on the exterior surface. Steps, kinks, and lattice imperfections could be active sites, but, we speculate, nucleation on these sites occurs only when the concentration of carbon atoms is large, i.e., at some elevated temperature and on nickel-rich substrates. Growth of these external nuclei cannot carry the metal particle, rather it would result in a veiling of the active sites for decomposition of benzene, thus inhibiting further deposition. Very little deposition in the intermediate region in Table 1, and the decreases in the deposition rates for nickel-rich powders in Fig. 5 could be explained by nucleation on the external surface. Type A carbon would thus be a consequence of very fast nucleation and succeeding growth of carbon on the external surface. According to this view, the competition between nucleation on the outer surface and at grain boundaries determines the gross rate. The above scheme is analogous to that proposed by Lobo *et al.* (7).

Nucleation at the grain boundaries exposed on the surface is reported frequently (11, 20, 22, 23) and seems reasonable, though we postulate that nucleation occurs to some extent inside the metal. But the details of the diffusion process, especially the chemical species that diffuses, are not certain and need further study.

### *Variation of Catalytic Activity with Alloy Composition*

The catalytic activity of alloys is a complicated phenomenon and widespread patterns of activity versus composition are reported (24, 25). Needless to say, such an activity pattern is related to the surface structure of the catalyst and the mechanism of each reaction. There seems to be two main factors relating to the activity pattern for type B deposition. First, cold rolled sheets tend to have smaller crystallites in some middle composition. This is seen in Table 2 and a similar trend is reported on



gold-palladium alloys (26). The smaller crystallites and therefore the larger population of grain boundaries are advantageous for type B deposition in the above scheme. Enhancement of the catalytic activity of nickel by alloying with copper is attributed to the increase in lattice defects (25, 27). The reduction of activity by heat treatment can be understood as the result of recrystallization of the smaller crystallites as indicated in Fig. 4.

The second and perhaps the more predominant factor manifests itself in the case of deposition on powders; the nickel-rich powders are more apt to be poisoned by carbon layer on the outer surface, while copper-rich substrates are poor catalysts for the decomposition of benzene, so that the activity has a maximum at some intermediate composition. The carbon fibers on copper-rich metals look sparse. This might mean that the surface of the metal particle occupied by copper atoms is not covered by carbon and assists gas molecules in approaching the decomposition site. But, for this explanation to hold, surface heterogeneity of alloy composition must be assumed.

There is a possibility that the surface composition of the alloy is different from the bulk. Recent reports showed that surface composition is closer to 1:1 ratio than the bulk composition (17, 25). But under present conditions, adsorbed carbon might catalyze the formation of nickel-rich surface layer within the long induction period for copper-rich powders. Using X-ray diffraction techniques, alloy segregation was carefully sought. In cases of 70 and 55% nickel powders, there was a slight indication that the lattice spacing of metal particles deviates to a larger one by 0.15% after they catalyzed the carbon formation. If the deviation were from the change in the composition (28), it corresponds to a copper-rich composition of bulk grain. But the above is not a sufficient evidence to state a nickel-rich surface layer. Miura *et al.* reported the segregation of copper and nickel at 375°C (29), but this temperature is close to that of unstable solution (30).

It was often discussed whether metal

carbide or reduced metal catalyzes the carbon formation (4, 11, 23, 29). If the metal carbide has something to do with the deposition, segregation of nickel would be necessary, at least for copper-rich alloys to have activity, since carbides of such alloys seem improbable.

#### *Effect of Hydrogen*

The enhancement of deposition rate by hydrogen has been reported in several cases (4, 14, 22, 31, 32), but this is not well understood. Lobo *et al.* suggested the acceleration of dehydrogenation and hydrogenolysis of hydrocarbon by hydrogen (7). As deposition on alloys is faster than on pure nickel, the rate of benzene decomposition on nickel cannot limit the overall rate. Another possible explanation, which is suggested for the effect of hydrogen on carburization of tungsten by hydrocarbons (33), is that hydrogen removes carbon patches on the surface. To rephrase it for the present case, hydrogen eliminates the carbon nuclei or embryos on the external surface, so that the surface is less poisoned. Further investigations on these points will be undertaken.

#### REFERENCES

1. KEHRER, V. J., JR., AND LEIDHEISER, H., JR., *J. Phys. Chem.* **58**, 550 (1954).
2. DAVIS, W. R., SLAWSON, R. J., AND RIGBY, G. R., *Nature (London)* **171**, 756 (1953).
3. WALKER, P. L., JR., AND THOMAS, J. M., *Carbon* **8**, 103 (1970).
4. WALKER, P. L., JR., RAKSZAWSKI, J. F., AND IMPERIAL, G. R., *J. Phys. Chem.* **63**, 133 and 140 (1959).
5. BANERJEE, B. C., HIRT, T. J., AND WALKER, P. L., JR., *Nature (London)* **192**, 450 (1961).
6. SAITO, T., AND GEJYO, T., *Carbon* **9**, 93 (1971).
7. LOBO, L. S., TRIMM, D. L., AND FIGUEIREDO, J. L., *Prepr. Int. Congr. Catal.*, 5th, Aug. 1972.
8. ROBERTSON, S. D., *Nature (London)* **221**, 1044 (1969).
9. ROBERTSON, S. D., *Carbon* **8**, 365 (1970).
10. LEIDHEISER, H., JR., AND GWATHMEY, A. T., *J. Amer. Chem. Soc.* **70**, 1206 (1948).
11. RUSTON, W. R., WARZEE, M., HENNAUT, J., AND WATY, J., *Carbon* **7**, 47 (1969).
12. BAIRD, T., FRYER, J. R., AND GRANT, B., *Nature (London)* **233**, 329 (1971).

13. BAKER, R. T. K., BARBER, M. A., HARRIS, P. S., FEATES, F. S., AND WAITE, R. J., *J. Catal.* **26**, 51 (1972).
14. TESNER, P. A., ROBINOVICH, E. Y., RAFALKES, I. S., AND AREFIEVA, E. F., *Carbon* **8**, 435 (1970).
15. HOFER, L. J. E., STERLING, E., AND MCCARTNEY, J. T., *J. Phys. Chem.* **59**, 1153 (1955).
16. YAMAKAWA, K., MS thesis, Tohoku University, 1969.
17. SINFELT, J. H., CARTER, J. L., AND YATES, D. J. C., *J. Catal.* **24**, 283 (1972).
18. MAIRE, J., AND MÉRING, J., in "Chemistry and Physics of Carbon" (P. L. Walker, Jr., Ed.), Vol. 6, p. 125. Dekker, New York, 1970.
19. KARU, A. E., AND BEER, M., *J. Appl. Phys.* **37**, 2179 (1966).
20. PRESLAND, A. E. B., AND WALKER, P. L., JR., *Carbon* **7**, 1 (1969).
21. REYNOLDS, P. W., *J. Chem. Soc.* **1950**, 265.
22. LOBO, L. S., AND TRIMM, D. L., *J. Catal.* **29**, 15 (1973).
23. RENSHAW, G. D., ROSCOE, C., AND WALKER, P. L., JR., *J. Catal.* **22**, 394 (1971).
24. MOSS, R. L., AND WHALLEY, L., in "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. **22**, p. 115. Academic Press, New York, 1972.
25. TAKASU, Y., AND SHIMIZU, H., *J. Catal.* **29**, 479 (1973).
26. CLARKE, J. K. A., AND RAFTER, E. A., *Z. Phys. Chem. (Frankfurt)* **67**, 169 (1969).
27. ONO, M., TAKASU, Y., NAKAYAMA, K., AND YAMASHINA, T., *Surface Sci.* **26**, 313 (1971).
28. CRATTY, L. E., JR., AND RUSSELL, W. W., *J. Amer. Chem. Soc.* **80**, 767 (1958).
29. MIURA, Y., UCHIJIMA, T., AND MAKISHIMA, S., *Kogyo Kagaku Zasshi* **71**, 86 (1968).
30. VAN DER PLANK, P., AND SACHTLER, W. M. H., *J. Catal.* **12**, 35 (1968).
31. TAMAI, Y., NISHIYAMA, Y., AND TAKAHASHI, M., *Carbon* **7**, 209 (1969).
32. BENEVOLENSKAYA, G. V., AND KEL'TSEV, V. V., *Gaz. Prom.* **10**, 32 (1965).
33. BOUDART, M., OLLIS, D. F., AND HARRIS, G. W., *Trans. Faraday Soc.* **65**, 519 (1969).