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Filamentous Carbon Growth on Nickel–Iron Surfaces: The Effect of Various Oxide Additives

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Controlled atmosphere electron microscopy has been used to follow the growth of filamentous carbon on Ni–Fe surfaces from the catalyzed decomposition of acetylene. Included in this investigation has been an examination of the manner by which various oxide additives, including SiO_2, Al_2O_3, TiO_2, WO_3, Ta_2O_5, and MoO_3, modify the growth characteristics of filaments from the alloy. It was found that all the oxides suppressed growth of this form of carbon at temperatures <620°C. Above this temperature only WO_3, Ta_2O_5, MoO_3, and SiO_2 exerted any influence, with the latter being the most effective inhibitor. A possible classification for the role by which various additives effect the growth rate of filamentous carbon is presented.

INTRODUCTION

In spite of the fact that carbon deposition is one of the major sources responsible for the loss of catalytic activity of many supported metal systems, it is surprising to find that there are very few reports in the literature relating to attempts at minimizing this effect.

Information that is available invariably pertains to the protection of large scale plant rather than to small metallic particles. A number of workers have found that sulfur can retard carbon formation (*1–3*). Bennett *et al.* (*4*) made a detailed study of the inhibition of carbon deposition, produced from decomposition of acetone on stainless steel, Fe_3O_4 and Cr_2O_3, by sulfiding and by the continuous addition of sulfur compounds to the gas phase. Sulfiding reduced and in some instances prevented carbon deposition on Fe_3O_4. Unfortunately this treatment did not affect deposition on Cr_2O_3. One could not, however, envisage using such a treatment on a universal scale for supported catalyst systems. Karcher and Glaude (*3*) have also demonstrated that deposition of silane onto iron and steel surfaces brought about an appreciable reduction in the formation of carbon from CO/H_2 mixtures. There are reports relating to the use of aluminum and aluminum alloys on iron-containing surfaces to improve the resistance to carbon formation on exposure to hydrocarbons at 400–1100°C (*5*). We have only found one reference devoted to the use of titanium, which indicates that alloys containing this metal exhibit low carbon deposition characteristics when exposed to hydrocarbons at 800°C (*6*).

It should be appreciated that in the majority of the work cited above no indication is given as to which form of carbon the various treatments are claimed to suppress. In the present study we have limited our investigation to studying the inhibition of filamentous carbon growth. This form of carbon is produced by the catalytic decomposition of carbon containing gases on small metal particles (*7*). A mechanism has been postulated to account for the growth of filamentous carbon (*8, 9*) which depends on diffusion of carbon through the metal particle from the hotter leading face on which hydrocarbon decomposition occurs to the cooler trailing faces at which carbon is deposited from solution. Carbon remaining at the leading particle surfaces migrates around the particle to constitute the wall of the filament, which has a different texture from the deposited material forming the core. Growth ceases when the leading face

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is covered by a layer of carbon built up as a consequence of rate control by the carbon diffusion process. A major criticism of this mechanism is that it fails to account for the finding of filaments produced by pyrolysis of methane, an endothermic process (*10*).

Our strategy has been to examine the possibility of inhibiting filamentous carbon formation by the introduction of additives to the catalyst particles, which might reduce the rate of the crucial steps involved in the growth process, i.e., carbon solubility or carbon diffusion through the catalyst particle. In this paper we shall report on the effect of treating Ni–Fe, a very active catalyst, with SiO_2, Al_2O_3, TiO_2, WO_3, Ta_2O_5, and MoO_3. The additives have been designated as oxides, since this was their initial form, however, this may not be the form once they are incorporated in the catalyst particles. A possible classification for the role by which these additives effect the growth rate of filamentous carbon will be discussed.

EXPERIMENTAL

The major technique used in this work was controlled atmosphere electron microscopy (*11*). At the termination of some experiments specimens were subsequently examined in the Philips EM 400 high-resolution transmission electron microscope, which when operated in the STEM mode enabled analysis to be performed on individual particles down to 40 nm in size.

In these experiments two different types of specimens were employed: Ni–Fe in the form of discrete particles supported on electron transparent sections of graphite or silica and Ni–Fe deposited as a thin film onto the surface of a nickel electron microscope grid which when heated resulted in nucleation of the film to produce particles. Silica films and transmission sections of a single crystal graphite were prepared in an identical manner to that previously described (*9*). Nickel electron microscope grids were first degreased in acetone and then washed in deionized water, before spot welding across the specimen hole in the platinum heater ribbon.

Equal amounts of high-purity iron (99.993% purity) and nickel (99.97 purity) wires were coevaporated onto the specimens at 5×10^{-6} Torr from a heated tungsten filament to produce a continuous film of mixed metal about 5 nm thick. In some experiments various additives were introduced onto the grid specimens. Aluminum and titanium were vacuum deposited as the metals: tungsten, tantalum, and silicon by vacuum evaporation of WO_3, Ta_2O_5, and SiO_2/Si powders, respectively, from a tungsten boat; and molybdenum by passing a high current through a molybdenum filament so that it fused to deposit a continuous film of metal about 0.5 nm thick. All these materials were introduced at a residual presure of 5×10^{-6} Torr. In order to assure intimate contact between the nickel–iron and the additive, all grid type of specimens were preheated in oxygen at 825°C for 1 hr prior to reaction with acetylene so that the uppermost layers were converted to oxides, and diffusion of some of the additive into the bulk metal was possible.

The gases used in this study, acetylene, hydrogen, and oxygen, were obtained from Scientific Gas Products, Inc. with stated purities of >99.5% and were used without further purification.

RESULTS

A. *Nickel–Iron-Catalyzed Decomposition of Acetylene*

It was found that if Ni–Fe films, supported on either graphite or silica, were heated directly in 2.0 Torr acetylene then the resultant particle nucleation was not very satisfactory, due to the accumulation of carbon on the surface. Excellent particle formation was obtained, however, if this process was performed in 1.0 Torr H_2. Providing the nucleation temperature had been maintained below 800°C then on subsequent exposure to acetylene both the supported systems exhibited identical behavior up to this temperature.

The first clear signs of carbon deposition were apparent at 480°C and this took the form of filamentous carbon growth, individual filaments being 5 to 50 nm diameter and up to 300 nm in length. As the temperature was raised, both the size and number of filaments being produced increased. The manner by which the filaments grew was similar to that observed in previous studies. A metal catalyst particle was located at the growing end of the filament and, during the reaction, was carried away from the support surface by the growth process. With the Ni–Fe/graphite system, the formation of filamentous carbon proceeded quite smoothly up to 925°C. At this temperature the amount of amorphous carbon collecting on the specimen became so heavy that most surface features were obscured. A major departure from this behavior was observed for Ni–Fe/silica specimens at temperatures in excess of 800°C, which is described in a later section.

In another series of experiments the form of the specimen was changed to that of a nickel grid onto which a film of Ni–Fe had been introduced. These specimens were too thick to allow penetration by the electron beam so that observations were limited to following the changes occurring at edges. When this system was heated in 2 Torr acetylene the original smooth surface took on a ragged appearance at 475°C. This behavior preceded the formation of carbon filaments at the same temperature. The filament characteristics were identical to those which grew from the supported metal system, showing an increase in growth rate and average size as the temperature was raised. Figure 1 is a transmission electron micrograph showing the typical appearance of filaments which had formed on the edge of a grid after 5 min reaction in a 2 Torr acetylene at 800°C. Under these conditions filament widths were between 20 to 300 nm and length up to 100 μm. At 927°C, growth was so prolific that it was impossible for the electron beam to penetrate the mass of accumulated deposit. Experiments performed on the bare nickel grids demonstrated that in this case the onset of filamentous growth did not take place until 700°C and that the amount of carbon deposited was far less than from Ni–Fe after comparable times at the same temperature.

From these studies it has been possible to obtain quantitative kinetic data on the growth of the filaments. The growth rate data where SiO_2 is absent, or believed not to be exerting any influence on the process, i.e., conditions where SiO_2 had not diffused into Fe–Ni particles, can be expressed in the form of an Arrhenius relationship, log filament growth rate against $1/T$ (Fig. 2). In order to overcome variations in rate with particle size, all measurements are based on 30-nm-diameter catalyst particles. These determinations were made over constant growth rate regions and each point represents the average of at least 10 filaments at each temperature. From the slope of this line, an apparent activation energy of 33.6 ± 4 kcal $mole^{-1}$ has been estimated for the process.

B. Influence of Silica on the Nickel–Iron/Acetylene Reaction

When Ni–Fe silica specimens were treated in 2 Torr acetylene at temperatures above 800°C several changes in the growth characteristics of filaments were apparent. Both the linear filament growth rate and the length to which they grew before termination was drastically reduced compared to that of the unadulterated system. A more subtle discovery was the observation of a sudden reduction in the electron scattering density of the filaments, suggesting that less material was diffusing through the catalyst particles to form the inner core of the filaments. Further, it was found that if the initial particle nucleation process on silica was performed at temperatures >800°C, then on subsequent exposure to acetylene the rate of formation of filaments was reduced at all temperatures, relative to that from the Ni–Fe/graphite system. More-

FIG. 1. Transmission electron micrograph showing the appearance of carbon filaments from Ni–Fe/acetylene at 800°C.

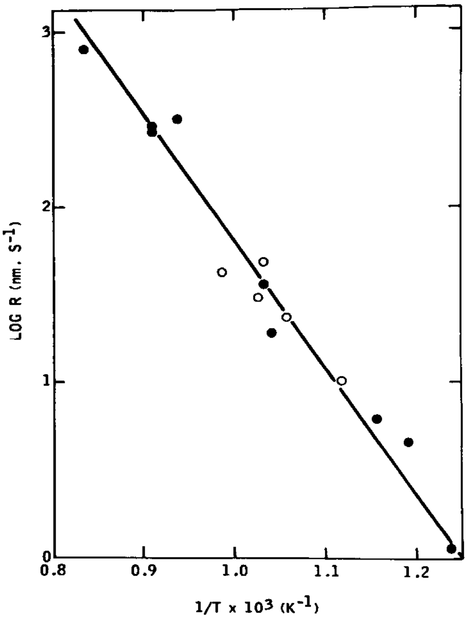

FIG. 2. Arrhenius plot for filamentous carbon growth from Ni-Fe-catalyzed decomposition of 2 Torr acetylene: ●, Ni–Fe/C_2H_2; ○, Ni–Fe + SiO_2/C_2H_2.

over, in this case, the onset of filament formation did not occur until about 675°C.

The grid type of experiment was extended to include an examination of the manner by which SiO_2 additions to the metal alloy surface modified subsequent carbon formation. SiO_2 was deposited in one of two arrangements, either (a) directly on top of the Ni–Fe film, or (b) interposed between the Ni grid and the Ni–Fe film.

When specimens in configuration (a) were heated directly in acetylene, carbon filament growth was not detected until 620°C, and then only in isolated patches on the surface. Growth of this form of carbon became more prolific as the temperature was raised to 755°C, but tended to slow down quite abruptly at higher temperatures, approximately 800°C.

In contrast there did not appear to be any inhibiting effect of SiO_2 on filament growth below 800°C when specimens in configuration (b) were treated under similar conditions. At temperatures >800°C both types of specimens exhibited similar behavior. The most dramatic effect was seen when specimens were preheated in oxygen at 825°C and then reacted in acetylene. In this case both forms of specimen showed identical behavior; some short filaments, growing at a very slow rate, were first seen at 675°C. As the temperature was raised, it became evident that both the size and growth rates of filaments were greatly reduced over that where SiO_2 was absent from the system. This feature can be best appreciated by comparison of the deposit in Fig. 3, a micrograph taken after hydrocarbon treatment at 800°C of a Ni–Fe/SiO_2 specimen, with Fig. 1, a Ni–Fe specimen reacted under identical conditions for the same period.

Quantitative data are presented in Fig. 4 for the linear increase in filament length with time from (A) Ni–Fe, and (B) Ni–Fe + SiO_2 preheated in O_2 at 825°C, during reaction of 30-nm-diameter catalyst particles with 2 Torr acetylene at 680°C. Both curves are sigmoid in shape, characteristic of a process where a catalyst is gradually poisoned. Two major differences are evident; the reduction in filament growth rate and ultimate length in the presence of added SiO_2. Typical dimensions of filaments produced on Ni–Fe/SiO_2 specimens when growth ceased at 800°C were 5 to 60 nm in width and 0.1 to 2.0 μm in length.

The influence of SiO_2 on the growth rate of carbon filaments from the Ni–Fe/C_2H_2 system is demonstrated emphatically in Fig. 5. Here, the logarithm of the average maximum growth rate of filaments produced from 30-nm-diameter catalyst particles is plotted as a function of temperature. It is clear that in systems where SiO_2 is absent or where conditions have not been attained that would result in the oxide being incorporated in the catalyst, there is a fairly rapid rise in the growth rate with temperature. When Ni–Fe + SiO_2 specimens were reacted directly in the hydrocarbon a dramatic falloff in filament growth rate occurs as the reaction temperature approaches 800°C, and above 820°C only a slight

FIG. 3. Transmission electron micrograph showing the appearance of carbon filaments from Ni–Fe + SiO_2/acetylene at 800°C.

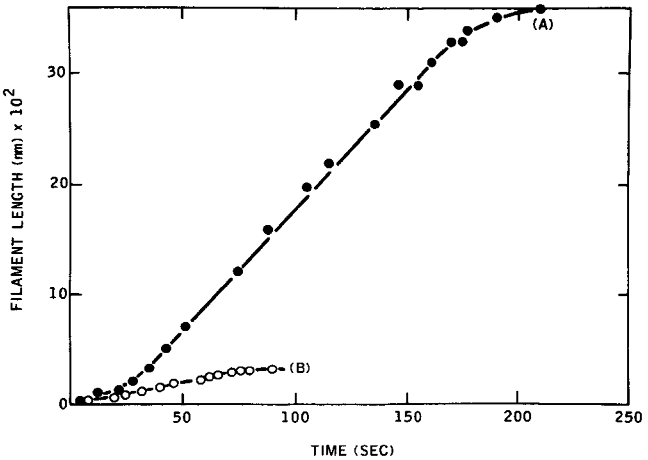

FIG. 4. Growth rate curve for filaments produced from 30-nm-diameter catalyst particles with 2 Torr acetylene at 680°C. (A) Ni–Fe, and (B) Ni–Fe + SiO_2 preheated in O_2 at 825°C.

change in rate is observed. When the same system was preheated in O_2 at 825°C prior to reaction with acetylene, inhibition of filament formation is seen at all temperatures.

Finally, postreaction X-ray energy dispersive chemical analysis of spent catalyst particles confirmed that SiO_2 was incorporated in those particles where Ni–Fe + SiO_2 particles had been treated at temperatures >800°C. The amount of Si found in such particles varied from 1 to 5%.

C. Influence of Alumina and Titania on the Nickel–Iron/Acetylene Reaction

The form of the specimen used in these experiments was the grid arrangement. Many of the features exhibited by these additives on the carbon deposition reaction were similar and so to avoid repetition, the results from these two systems will therefore be treated collectively. When specimens were treated in 2 Torr acetylene no obvious changes in the appearance of the

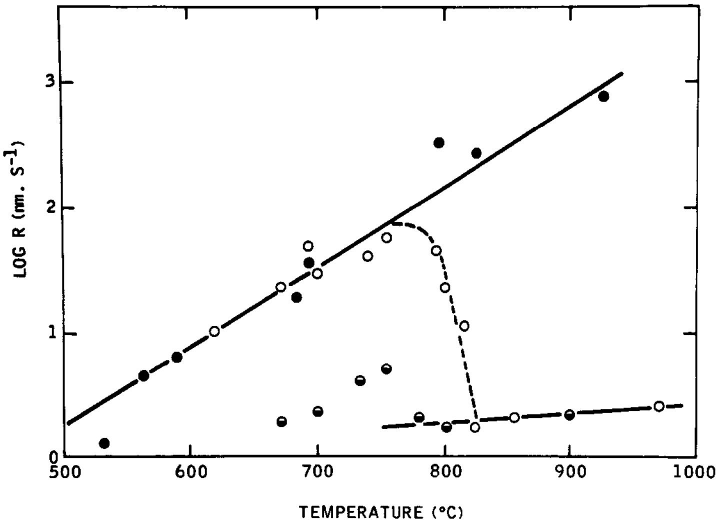

FIG. 5. Variation of log filament growth rate with temperature: ●, Ni–Fe/C_2H_2; ○, Ni–Fe + SiO_2/C_2H_2; ◒, Ni–Fe + SiO_2 preheated in O_2 at 825°C for 1 hr/C_2H_2.

surface was observed until the temperature reached 650°C. At this stage the first signs of very sparse filament growth was detected; the average dimensions of the filaments were 7 nm width and 45 nm length. Raising the temperature produced dramatic changes in these specimens, which are illustrated schematically in Fig. 6. Parts of the oxide coating started to disrupt, exposing the bare metal surface to the gas and almost immediately prolific filament formation occurred. Once initiated, this action became self perpetuating; as filaments formed they caused further break-up of the protective oxide layers, exposing a fresh supply of potential catalyst particles. The rate at which this action spread to cover the entire surface was accelerated by increasing the temperature.

The qualitative features of the filaments produced from the two systems showed some differences in characteristics. Those formed from the Ni–Fe + Al_2O_3 reaction with the hydrocarbon tended to be similar to filaments which grew on the virgin metal surface. On the other hand many of the carbon filaments formed in the presence of titania were in a spiral conformation, where the catalyst particle was located within the filament, which grew from two faces of the particle in opposite directions. An example of this type of growth can be seen in the micrograph, Fig. 7.

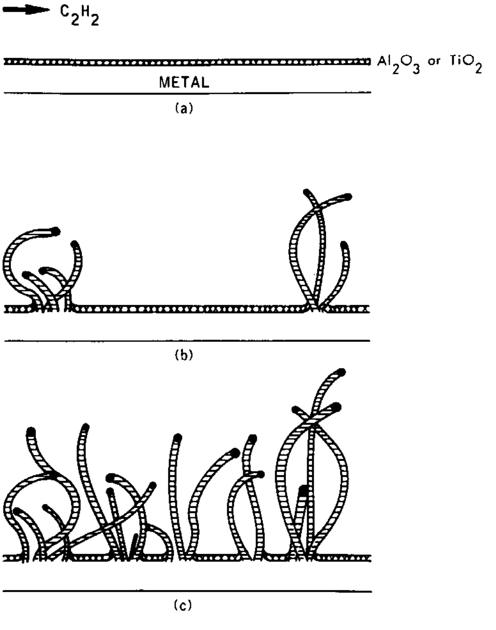

FIG. 6. Stages in the failure of alumina and titania coatings on a Ni–Fe surface.

From the quantitative measurements of filament growth rates at various temperatures it has been possible to evaluate the growth kinetics of filaments in the presence of Al_2O_3 and TiO_2. Inspection of Fig. 8, a plot of the logarithm of the maximum growth rate of filaments formed by 30-nm-diameter catalyst particles against the reciprocal of absolute temperature, clearly shows that neither oxide exerts any significant influence on the rate-determining step of the individual filaments. The apparent activation energies derived from these slopes being 32.9 ± 4 kcal mole^{-1} for the Al_2O_3 system and 31.6 ± 3 kcal mole^{-1} for the TiO_2 system, which, within experimental error, is the same as that derived from the virgin surface.

D. Influence of Tungsten, Tantalum, and Molybdenum Oxides on the Nickel–Iron/Acetylene Reaction

When nickel–iron specimens treated with these three oxides were heated in 2 Torr acetylene they showed similar behavioral patterns, differing only in the temperatures at which various events occurred. For this reason they will be dealt with together and any variations from this general discription will be highlighted separately.

The first signs of filamentous carbon growth occurred at 685°C ± 15°C. Traversal of the edges of the specimens showed that such growth was starting to develop in a few isolated regions, and activity was restricted to catalyst particles in the size range, 2.5 to 20 nm. These particles had formed at 400–500°C as a result of nucleation of the metal films. The only major change which occurred as the temperature was gradually increased to 865°C was that the width of newly formed fila-

FIG. 7. Transmission electron micrograph showing the spiral form of filaments produced by Ni–Fe + TiO_2 catalyst particles after exposure to 2 Torr acetylene at 825°C.

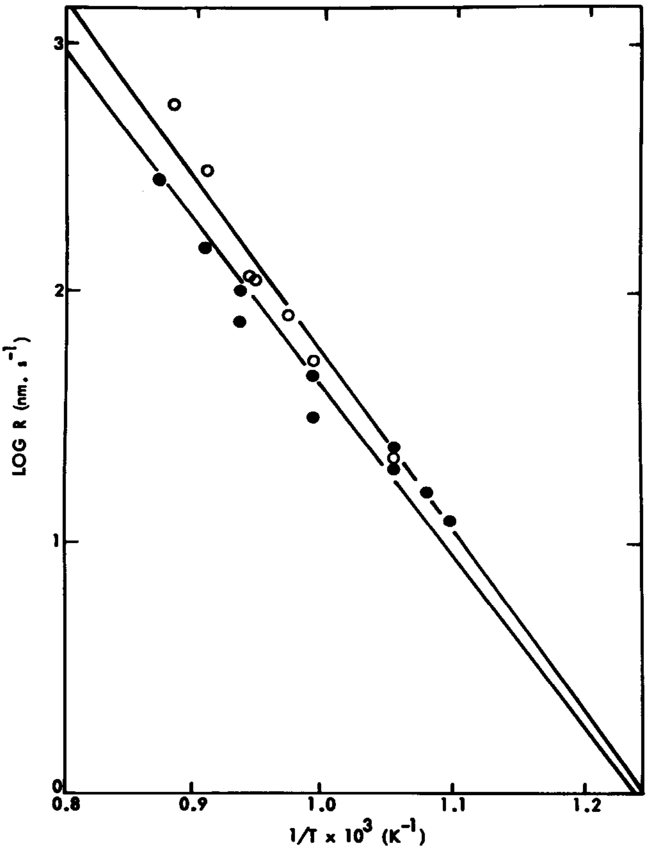

FIG. 8. Arrhenius plots for filamentous carbon growth from (a) ○, Ni–Fe + Al_2O_3/C_2H_2; and (b) ●, Ni–Fe + TiO_2/C_2H_2.

ments tended to increase, thus enabling a more precise identification of their growth characteristics. Careful examination of many filaments revealed that the inner core was transparent toward the electron beam, and the smaller growths gave the appearance of being hollow. In all other respects, however, at temperatures up to 865°C, the qualitative features of the filaments were identical to those formed on the virgin metal surface.

A major departure from the conventional filament growth pattern was found at temperatures above 865°C for both the Ni–Fe + WO_3 and Ni–Fe + Ta_2O_5 systems, Ni–Fe + MoO_3 continuing to produce filaments in the normal mode. This deviation took the form of finer secondary filaments, which were produced as a result of fragmentation of some of the catalyst particles at the heads of the larger filaments present. These secondary structures grew at a much faster linear rate than that of the main filament and were formed by two modes. In one case, small fragmentary particles were split off continuously from the parent particle so that the filaments created from such particles formed at intervals along the edges of the main filament producing a spinal conformation. It was apparent that as this process proceeded the original particle became depleted in material and as a consequence the main filament became tapered. In the other situation, fragmentation of the parent particle took place in a single explosive act generating numerous smaller particles. Although these particles continued to catalyze filamentous growth, their activity was relatively short-lived. An example of this phenomenon is shown in the sequence in Figs. 9A–D.

Quantitative kinetic analysis of a number of recorded reaction sequences enabled an evaluation of the growth kinetics of carbon filaments in the presence of these three oxides. An Arrhenius plot of the results obtained from 30-nm-diameter catalyst particles is shown in Fig. 10. From the slopes of these lines apparent activation energies of 32.8 ± 3.5 kcal mole^{-1} (WO_3), 30.5 ± 3 kcal mole^{-1} (Ta_2O_5), and 30.9 ± 3 kcal mole^{-1} (MoO_3) have been estimated for the filament growth process.

A fairly rigorous postreaction examination was conducted on spent catalyst particles from the Ni–Fe + WO_3/C_2H_2 system. X-Ray energy dispersive chemical analysis of such particles confirmed that WO_3 was incorporated in the particles. High-resolution transmission electron microscopy also demonstrated that deactivated particles were encapsulated in a thin layer of graphite, approximately 2 nm thick, which extended along the filament axis in the form of a skin surrounding a nongraphitic inner core (*19*).

DISCUSSION

The CAEM studies have shown that the behavior of supported Ni–Fe particles toward acetylene is identical to that where the alloy is initially present as a thin film on a bulk metal surface. Moreover, it is apparent from the data presented in Table 1 that Ni–Fe is a much more active catalyst for filamentous carbon growth than either of the component metals. This feature may be related to the fact that addition of Ni to Fe stabilizes the γ-form of Fe down to 350°C (*12*). When the metal is in the pure state, the transition of α- to γ-form does not occur until temperatures in excess of 900°C (*12*). These two phases have different structures, α- is B.C.C. and γ- is F.C.C., and as a consequence exhibit different carbon diffusion characteristics. The activation energies for diffusion of carbon through α-Fe being 16.1 kcal mole^{-1} (*13*), and through γ-Fe, 33.3-39.5 kcal mole^{-1} (*14*). This conclusion may not hold for very high reaction temperatures, since Schnaas and Grabke (*20*) reported that at 1050–1100°C an alloy with a Ni/Fe = 4/1 had the optimum resistance to carburization, a process which is controlled by carbon diffusion.

Comparison of the activation energy for filament growth in this system with that for diffusion of carbon through Ni-Fe is also presented in Table 1. The excellent agreement between these values lends further support to the postulate that diffusion of carbon through the catalyst particle is the rate-determining step in filamentous carbon growth (*8*).

From this work it is also evident that treatment of Ni–Fe surfaces with various oxides can have a profound effect on the catalytic formation of carbon filaments when the alloy is subsequently heated in

TABLE 1

Comparison of the Catalytic Behavior of Nickel–Iron, Nickel, and Iron in the Formation of Filamentous Carbon from 2 Torr Acetylene

Catalyst	Onset temperature (°C)	Structure	Activation energy for Diffusion of carbon (kcal mole^{-1})	Activation energy for Catalyzed filamentous carbon growth (kcal mole^{-1})
α-Iron	650	B.C.C. (2.866 Å)	10.5–16.5 (13)	16.1 (9)
Nickel	700	F.C.C. (3.524 Å)	33.0–34.8 (15)	34.7 (8)
Nickel–iron	470	F.C.C. (3.571 Å)	34.0 (16)	33.6 ± 4.0

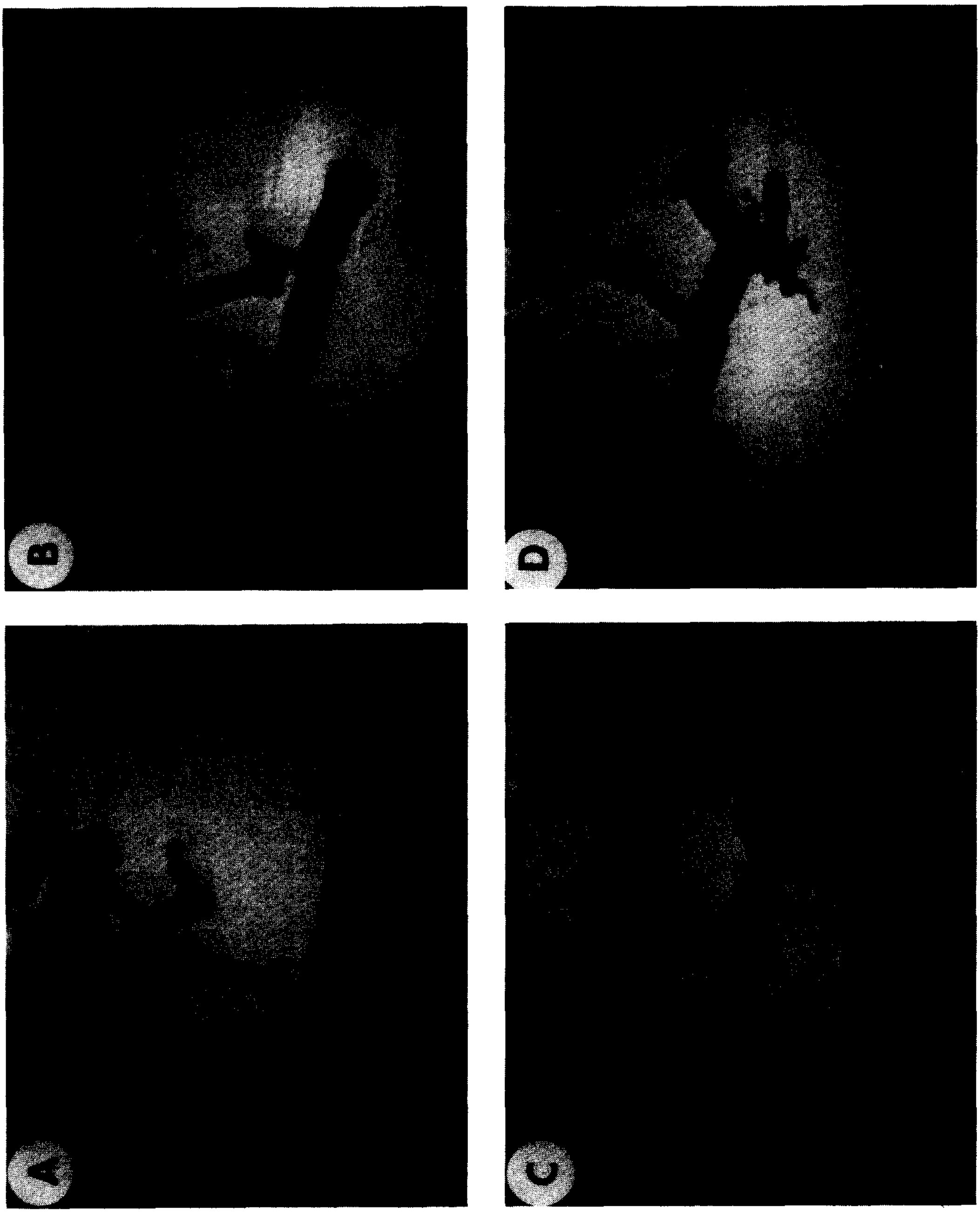

FIG. 9. (A–D) Sequence showing catalyst particle fragmentation and subsequent secondary filament growth.

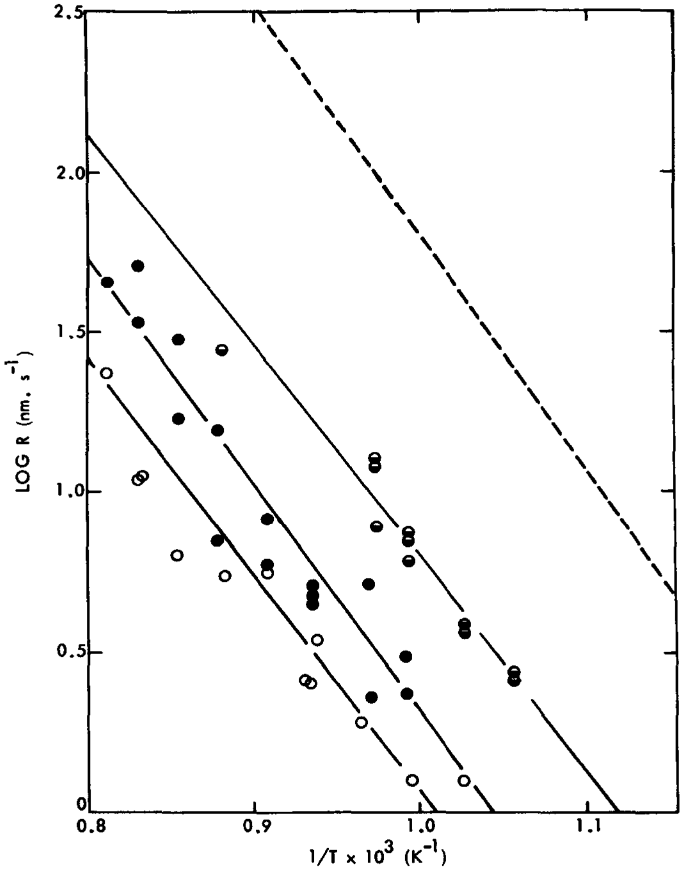

FIG. 10. Arrhenius plots for filamentous carbon growth from (a) ○, Ni–Fe + MoO_3/C_2H_2; (b) ●, Ni–Fe + WO_3/C_2H_2; and (c) ⊖, Ni–Fe + Ta_2O_5/C_2H_2; dotted line for virgin specimen.

acetylene. There is ample evidence to suggest that the majority of the oxides used in this work function as inhibitors for the growth of this form of carbon by their ability to become incorporated in the catalyst particles.

Unequivocable proof comes from the STEM examination for the cases of SiO_2 and WO_3 treatments of Ni–Fe surfaces which showed the presence of both species in catalyst particles located at the ends of the filaments produced on such specimens. Somewhat less direct indications are seen from the change in physical characteristics of filaments formed following addition of the oxides, compared to those grown on the virgin alloy. It was the anomalous behavior of Ni–Fe + SiO_2 at about 800°C which led to the extremely important discovery that the oxide inhibits filament growth. Departures from normal behavior have previously been observed when Fe, Co, or Cr supported on silica were heated in acetylene to temperatures around 800°C (*9*) and it was suggested that incorporation of silica into the catalyst particles was responsible for promoting such effects. The observation that filaments produced in the presence of titania were often in the form of spirals, where the catalyst was located within the filament is consistent with the notion that titania is contained in the particle. This type of filament conformation is rare, the only previous report of its occurrence being from the $Fe–Sn/C_2H_2$ system (*17*).

The tendency of particles to fragment during filament formation coupled with the finding of a reduction in the electron scattering density of the inner core of filaments are anomalies, which point to a subtle change in the nature of the catalyst particles in many of these systems.

A comparison of the kinetic parameters and other data obtained in this study, summarized in Table 2, indicates that the rate of formation of filamentous carbon from the Ni–Fe/C_2H_2 system varies quite markedly with the different additives. Alumina appears to provide excellent protection up to 650°C, however, once spalling of the oxide film occurs the rate of growth reverts back to that of the pure system. Perhaps the most intriguing result is that, with the exception of SiO_2, none of these additives appears to alter the activation energy for the filament growth process, i.e., they do not affect the rate-determining step, the diffusion of carbon through the catalyst particle.

It is possible that once the oxides are incorporated within the catalyst their role is that of a component for reducing carbon solubility in the particle. Available bulk metallurgical information supports this hypothesis for addition of Mo, Si, and W to the Fe–C binary system; as little as 1% W addition to Fe reduces carbon solubility by 50% (*18*). Unfortunately comparable data are not available for Ta, however, it is expected that this material should exert a similar qualitative effect. Moreover, there is no reason to suppose that the additives would behave any differently with the C–Fe-Ni ternary system.

From a consideration of the proposed model for carbon filament formation (*8*) one can readily predict the consequences of a reduction in carbon solubility in the catalyst on the subsequent filament growth characteristics. From a structural standpoint one would expect to see a reduction in the density of the inner core region and a resultant build-up of excess carbon at the particle surface, causing premature deactivation of the catalyst. It is also possible that introduction of these additives into Ni–Fe raises the effective Tammann temperature of the particles restricting the carbon transport process to the outer layers of the particle where enrichment in both Ni and Fe might occur. This behavior could not only account for the change in carbon diffusion geometry through the particle, but also for the gradual splitting off of smaller fragments and in some cases complete distruction of the original particles caused by a difference in thermal properties between the outer layer and inner core components of the particle.

A further ramification of the reduction in carbon solubility is that at any given temperature the rate of diffusion of those carbon species which did dissolve would also

TABLE 2

Effect of Various Additives on the Growth of Filamentous Carbon from Ni–Fe/C_2H_2

Additive	Onset temperature (°C)	Rate of filament growth at 850°C (nm s^{-1})	Apparent activation energy (kcal $mole^{-1}$)
None	480	413	33.6
Alumina	650	428	32.9
Titania	635	220	31.6
Tungsten oxide	700	12.6	32.8
Tantalum oxide	680	34.7	30.5
Molybdenum oxide	670	6.6	30.9
Silica	620	2.1	—

be reduced since the driving force for diffusion, the temperature gradient created in the particle, would not be a maximum, lacking the full contribution from the heat of solution of carbon in the alloy. All these features were observed experimentally, varying in degree with the different additives.

From the results of this study we are now in a position to propose a tentative classification of the roles of various additives on inhibition of filamentous carbon growth.

(i) Some materials provide a physical barrier toward hydrocarbon adsorption and decomposition on the metal surface, but spall at elevated temperatures, e.g., Al_2O_3 and TiO_2.

(ii) Other additives reduce carbon solubility in the metal catalyst particles, but have no effect on carbon diffusion through the particle, e.g., MoO_3, WO_3, and Ta_2O_5.

(iii) There are cases where an additive can reduce both the solubility of carbon and its diffusion through the catalyst particle, e.g., SiO_2.

It should be appreciated that these materials have been designated as oxides, since this was their initial form, however, there is no a priori reason why they should remain as oxides once they are incorporated within the catalyst particles. Unfortunately, there is no way at present of determining their precise state during the reaction, or what minimum quantity is required to achieve maximum effectiveness.

SUMMARY

It has been established that Ni–Fe is a very active catalyst for filamentous carbon formation from the decomposition of acetylene. We have demonstrated that this action can be inhibited by the incorporation of additives in the alloy particles. All additives investigated here suppressed the growth of this form of carbon at temperatures below 620°C. Above this temperature only Ta_2O_5, WO_3, MoO_3, and SiO_2 exert any retarding influence, with the latter being the most superior inhibitor.

REFERENCES

1. Berry, T. J., Ames, R. N., and Snow, R. B., *J. Amer. Ceram. Soc.* **39,** 308 (1956).
2. Schenck, H., and Maschlanka, W., *Arch. Eisenhuttenvsen* **31,** 271 (1931).
3. Karcher, W., and Glaude, P., *Carbon* **9,** 617 (1971).
4. Bennett, M. J., Chaffey, G. H., Myatt, B. L., and Silvester, D.R.V., A.E.R.E. Report R7408 (1973).
5. Hoppstock, F. H., Frech, K. J., and Hutchings, D. A., *Chem. Eng. News* **53,** 49 (1975).
6. Starshov, J. M., Ivanova, G. Ya., and Paimukhin, T. P., *Meft. Khim.* (*Kazan*) **2,** 67 (1974).
7. Baker, R. T. K., and Harris, P. S., *in* "Chemistry and Physics of Carbon" (P. J. Walker, Jr. and P. A. Thrower, Eds.), Vol. 14, pp. 83–165. Dekker, New York, 1978.
8. Baker, R. T. K., Feates, F. S., Barber, M. A., Harris, P. S., and Waite, R. J., *J. Catal.* **26,** 51 (1972).
9. Baker, R. T. J., Harris, P. S., Thomas, R. B., and Waite, R. J., *J. Catal.* **30,** 86 (1973).
10. Rostrup-Nielsen, Jr., "Steam Reforming Catalysts," p. 134. Teknisk Forlay A/S (Danish Technical Press, Inc.), Copenhagen, 1975.
11. Baker, R. T. K., *Catal. Rev.-Sci. Eng.* **19,** 161 (1979).
12. Hansen, M., "Constitution of Binary Alloys," 1958; Elliott, R. P., Suppl. 1, 1965; Shunk, F. A., Suppl. 2, 1969. McGraw Hill, New York.
13. Morgan, D. W., and Kitchener, J. A., *Trans. Faraday Soc.* **50,** 51 (1964); Grace, R. E., and Derge. G., *Trans. AIME* **212,** 331 (1958).
14. Kidin, I. N., Shcherbedinskii, G. V., Andryvsheckin, V. I., and Volkov, V. A., *Metalloved. Term. Obrab. Metal.* No. 12, 26 (1971).
15. Diamond, S., and Wert., C., *Trans. AIME* **239,** 705 (1967).
16. Smith, R. P., *Trans. Met. Soc. AIME* **236,** 1224 (1966).
17. Baker, R. T. K., Harris, P. S., and Terry, S., *Nature* (*London*) **253,** 37 (1975).
18. "Metals Handbook," Vol. 8, 1973. American Society for Metals.
19. Raghavan, M., Proc. 37th EMSA Meeting, San Antonio, Texas 484, 1979.
20. Schnass, A., and Grabke, H. J., *Oxid. Metals* **12,** 387 (1978).