coexisting phases from excellent to non-existent, as well as the sequential nature of reactions preceding diamond formation from simple solution to stable carbide formation, and, with respect to the latter, the formation of carbides of limited stability to those stable under the widest range of environment, suggests that the probability of a catalytic mechanism is questionable.

The strongest motive for the concept of catalysis probably has been the presence of the Ni_xC phase in synthetic diamond, since the most commonly used chemistry generally includes nickel. The great excess of dissolved carbon existing in a saturated solution prior to decomposition and diamond growth (Fig. 7 (a)) in comparison to residually included matter such as Ni_xC implies, however, that the latter simply represents an entrapped incidental nickel-carbon composition from the depleted solution which circumstantially has a crystal structure similar to that of diamond. The inclusion need not exercise an essential influence on diamond formation. The probability exists, in fact, that diamond may be influential in the crystallization of the Ni_xC (or Co_xC) since it has only been observed as an epitaxially included phase. That the latter does exert an influence upon diamond morphology has been mentioned earlier. The effect, however, appears to be an adverse one.

At higher temperatures of crystallization, it is observed that both the total yield of diamond and number of individual crystals generally is greater, whereas size and impurity content (non-carbide forming solvents) is lower. By analogy, these characteristics are similar to ordinary crystallization processes from chemical solution. The above can be interpreted as representing a rapid supersaturation as functions of temperature and reactant concentration resulting in widespread precipitation, nucleation and growth. The existence of lower concentrations of included matter can be taken to indicate simply a more complete local depletion of dissolved carbon independent of influence on diamond crystallization. Material transport is observed to be remarkably vigorous under conditions of high pressure and high temperature (Figs. 6 and 7(a)).

Several experiments have been conducted to test the concept of crystallization from solution. Reactions designed to precipitate the metal solvent from solution so as to induce a premature, controlled state of carbon supersaturation have been carried out. Success was achieved through precipitation of the metal as insoluble silicates, primarily as garnet-type compounds of cobalt, iron and manganese, respectively. Diamond in the form of colorless octahedra[1] could be crystallized in the region of secondary precipitant reactions, whereas in an adjacent area of the same experi-

[1] Due to the intimate and rapid initial crystallization, the various garnet precipitants commonly are observed both as intergrowths, overgrowths and inclusions within the diamond.

ment free from secondary precipitation, cube crystals of high impurity content were obtained. The results support the mechanism proposed.

Since the temperature of supersaturation and spontaneous crystallization can thus be controlled, by inference, pressure requirements also are subject to manipulation. The two, however, still must meet fundamental thermodynamic requirements for diamond stability.

Further experimentation performed to study the mode of diamond formation concerned studies on carbon solution, precipitation and recrystallization from non-metallic solvents. Several ammonium compounds were chosen. Examples have been given earlier. Successful solution and spontaneous precipitation have been successfully achieved. At pressures normally required for diamond growth, however, exceptionally high temperatures have been found necessary to achieve supersaturation (approximately 2000° C. and above). Pressure requirements for diamond at these temperatures are severe. Only single crystals of recrystallized graphite were obtained. These were, however, of excellent crystallinity and chemical purity.

An additional experiment was chosen to test the solution concept. In this case, a carbide former and non-carbide former constituted the metal solvents for carbon, with the idea being that the selected carbide former would form a stable compound at a lower temperature than carbon supersaturation could be achieved in either of the two metals. An added criterion was that the temperature of supersaturation of the carbide former be higher than that of the non-carbide former at any given pressure in the achievable diamond growth range. Nickel and chromium were chosen as qualifying solvents. A thermal gradient was imposed on the graphite-metal system with the higher temperature being in the graphite environment. The test was to determine whether the carbide former would precipitate dissolved carbon from the solution in the cooler portion of the metallic solvent; the result anticipated being a premature supersaturation of the non-carbide forming solvent (nickel) in the hotter zone at the graphite interface. The latter might be expected to occur as the result of the imposed concentration gradient on the dissolved carbon, thus inducing an accelerated diffusion rate (pressure and temperature held constant). The experiment succeeded and the objectives were confirmed. Figure 12 shows a cross sectional view of a recovered specimen. The needle-like phase in the central portion of the metallic zone is Cr_3C_2. It was observed that diamond could be crystallized at pressures and temperatures somewhat lower than normally encountered for nickel. Since the above situation is quite analogous to those which exist for commercial alloys such as inconel and nichrome, the explanation may also apply to them.

Solution mobility and lower carbon saturation temperatures for