

## X-RAY STUDY OF SYNTHETIC DIAMOND AND ASSOCIATED PHASES

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### ABSTRACT

Reaction products recovered from high-temperature/high-pressure diamond syntheses involving graphite and various metals have been studied principally by *x*-ray diffraction methods. Diamond single-crystal patterns show two distinct crystal types: Those with intergrown, metal-containing "satellite" phases (from Ni, Co, and inconel solvents); those free of such phases (from Mn and Fe). The two types are explained on the basis of structural fit and stability. Colored phases in the pyrophyllite alteration zone are identified, along with spessartite, almandite, and a new Co-containing garnet. The latter two may be intergrown with diamond. Various carbides and minor spinels are formed in the charge area.

Instrumentation developed for diamond synthesis presents a powerful tool for small scale simulation of geophysical conditions in the order of  $10^6$  psi. and  $2000^\circ$  C.

### INTRODUCTION

A particularly important aspect of mineralogical research involves a continuing effort to simulate various assemblages of natural environmental conditions. In many instances, this is somewhat akin to approaching infinity, mostly due to man's inability to substitute adequately for the time factor. In a few cases, nevertheless, man has actually succeeded in surpassing the products of nature, *e.g.*, ruby, sapphire, quartz, and there is no doubt that the list will be extended as crystal growth technology advances. The continuing development of new structural materials has made possible improved designs for experimental instrumentation to extend our capability in simulating environmental extremes. The relatively new high-temperature/high-pressure equipment is one of the most promising developments of this kind in recent years. Diamond has been synthesized for the first time (Anon. 1955), to be sure not of the quality or size found naturally, but this is not the important point. The mineralogical significance lies in the fact that a capability has been demonstrated for small scale simulation of geophysical conditions in the range of  $10^6$  psi. and  $2000^\circ$  C. The research possibilities for studying the effect of such conditions on a variety of geochemical associations are obviously enormous. This paper describes some results of an *x*-ray and optical study of reaction products from attempted diamond syntheses using graphite with each of the pure metals Ni, Co, Mn, Fe, Cr, Ta and Pt and with inconel.

### INSTRUMENTATION AND EXPERIMENTAL PROCEDURE

The supported, stepped piston-cylinder pressure chamber used for HP/HT reactions in connection with the present study was independ-

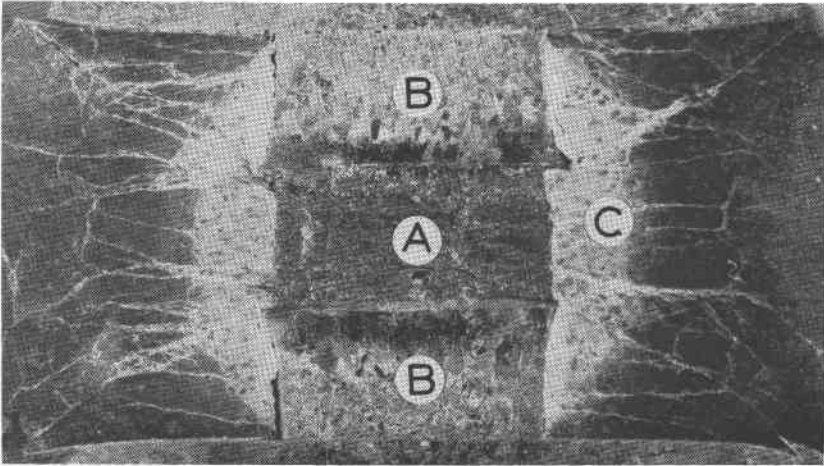


FIG. 1. Typical, reacted, axially-sectioned specimen capsule, showing graphite charge area, A, metal end plugs (in this case Ni), B, and pyrophyllite alteration zone, C. Diameter is 0.5 inch.

ently designed at this Laboratory and has been presented elsewhere (Giardini *et al.*, 1960; Giardini and Tydings, 1962). The specimen chamber geometry and processing details are the same as described in these references, and the reader is referred thereto for further data. Reacted cylindrical specimen capsules were ejected from the pressure chamber, mounted in leucite, and ground and polished to reveal an axial section. A typical, processed specimen is shown in Fig. 1; outside diameter is 0.5 inch. Areas of interest are in the graphite charge, A, in and around the metal end plugs, B, and in the pyrophyllite alteration zone, C. These areas were examined under a binocular microscope and minute samples probed for powder  $x$ -ray diffraction. Single crystals of diamond and secondary reaction phases were mounted for optical goniometric study and subsequent rotation and Weissenberg  $x$ -ray patterns. Supporting data were sought in some cases by emission spectroscopy and petrographic microscopy.

#### CHARGE-AREA REACTION PRODUCTS

*Diamond:* Diamonds were studied from syntheses using end plugs of the pure metals Ni, Co, Mn and Fe and with inconel. Single-crystal  $x$ -ray rotation patterns, mostly around the [110] axis, showed two distinct types of diamond, those with and those without a metal-containing "satellite" phase. The "satellite" phase has been studied extensively by Lonsdale *et al.* (1959) in the case of diamonds grown from Ni. These authors found

that an  $\text{Ni}_x\text{C}$  structure ( $x > 4$ ) was formed within, and parallel to, the diamond structure. Whereas the latter had a cell dimension of 3.567 Å, the metal-containing phase had a cell edge of 3.539 Å. Figure 2 is a rotation pattern of a typical Ni-grown diamond; the streaked "satellite" reflections are clearly seen on the high-angle side of their respective diamond reflections. Note that the (200) reflection (circled), which is not permissible in diamond owing to the  $d$  glide plane, is clearly visible in the "satellite" phase. The co-grown diamonds showed similar rotation patterns, the only difference being that the "satellite" phase gave a cell edge exactly equal to that of diamond, namely 3.567 Å, and the reflections of the two phases were coincident.

Diamonds from Ni and Co showed morphologies ranging from cubes through cube-octahedra to octahedra and colors from black to green to yellow to almost colorless. Dodecahedral faces were noted on some examples. Relationships among color, morphology and impurity content are described by Giardini and Tydings (1962) in the accompanying paper.

Diamonds grown from inconel ( $\sim 77\%$  Ni, 15% Cr, 6% Fe) showed one of two "satellite" phases, having cell dimensions of 3.547 and 3.555

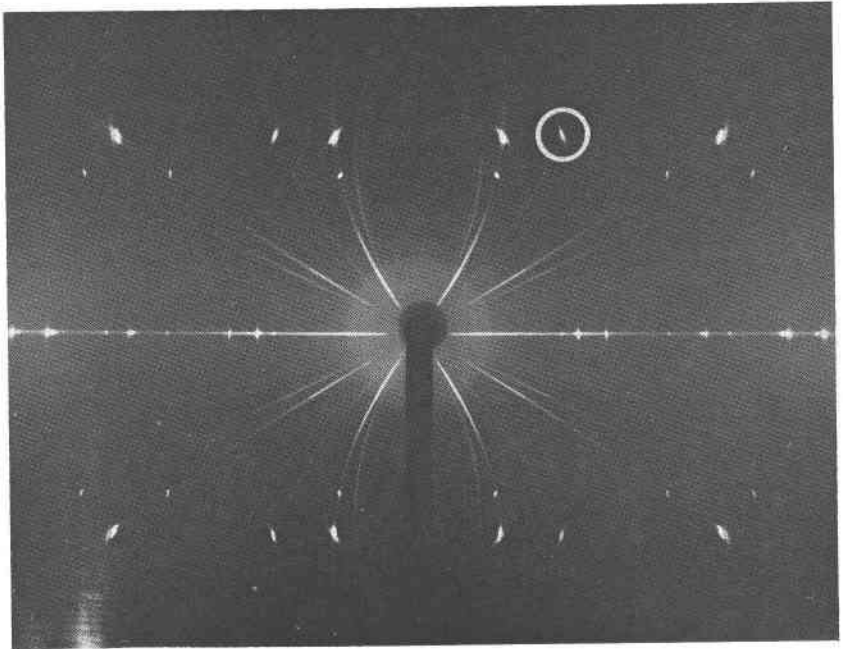


FIG. 2. Rotation pattern of Ni-grown diamond, showing "satellite" reflections on the high-angle side of diamond reflections. Note the presence of (200), circled.  $\text{FeK}\alpha$ , 13 hrs., [110] rotation.

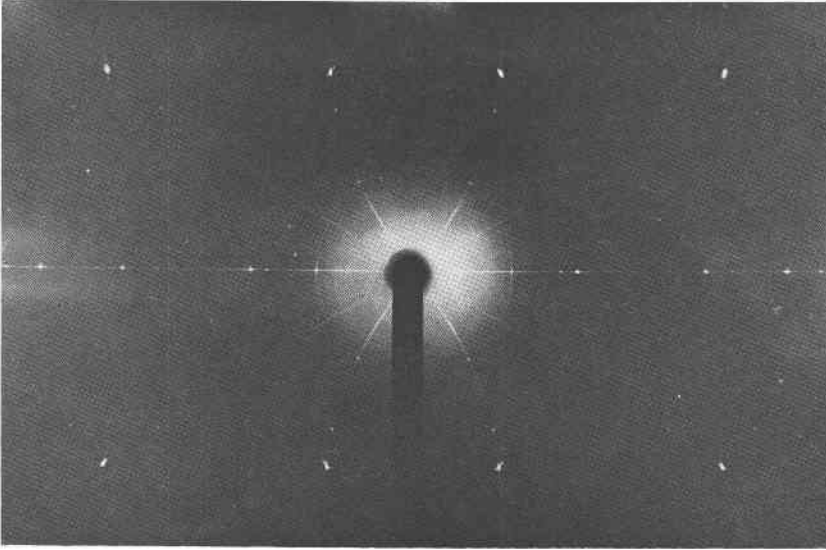


FIG. 3. Rotation pattern of Mn-grown diamond, showing absence of "satellite" reflections and (200). Note the (0002) graphite ring with nodes indicating octahedral preferred orientation. FeK $\alpha$ , 13 hrs., [110] rotation.

Å. The latter was associated with crystals having essentially a cube habit, whereas the former was found in crystals tending toward octahedra. Since diamond cubes form at a lower temperature than octahedra, it can be said that crystals having the larger "satellite" form at a lower temperature than those with the smaller "satellite." The "satellite" phases in the case of inconel-grown diamonds are most probably associated with the metal eutectic compositions at elevated pressures; the exact nature of such compositions would require a high-pressure study of the Fe-Cr-Ni ternary system. Colors and morphologies of inconel diamonds are similar to those obtained with Ni and Co. One particular yellow-green inconel diamond, however, showed the form {113}, in addition to {111}, {100} and {110}.

Diamonds obtained using Ni, Co or inconel, as would be expected from their intergrown, metal-containing "satellite" phases, were found in the metal end plugs at the metal-graphite interfaces. In distinct contrast, diamonds formed with Mn or Fe end plugs were found directly in the central graphite charge area. Such diamonds showed no  $x$ -ray evidence whatsoever of a "satellite" phase. A rotation pattern of a diamond obtained with Mn is shown in Fig. 3. Note the absence of (200), as required for pure diamond. The inner ring of reflections in the figure is (0002) of graphite, with the nodes indicating preferred orientation of the graphite

inclusions along diamond octahedral planes. More often the "graphite ring" either showed no preferred orientation or was absent completely. A rotation pattern of natural diamond is shown in Fig. 4 for comparison. Diamonds from Fe or Mn were colorless or contained macroscopic, black inclusions (graphite). The habit was generally octahedral, indicating higher temperatures of formation than in the case of Ni, Co and inconel.

An obvious question at this point concerns why "satellite" phases are observed with diamonds grown from some metals and not with others.

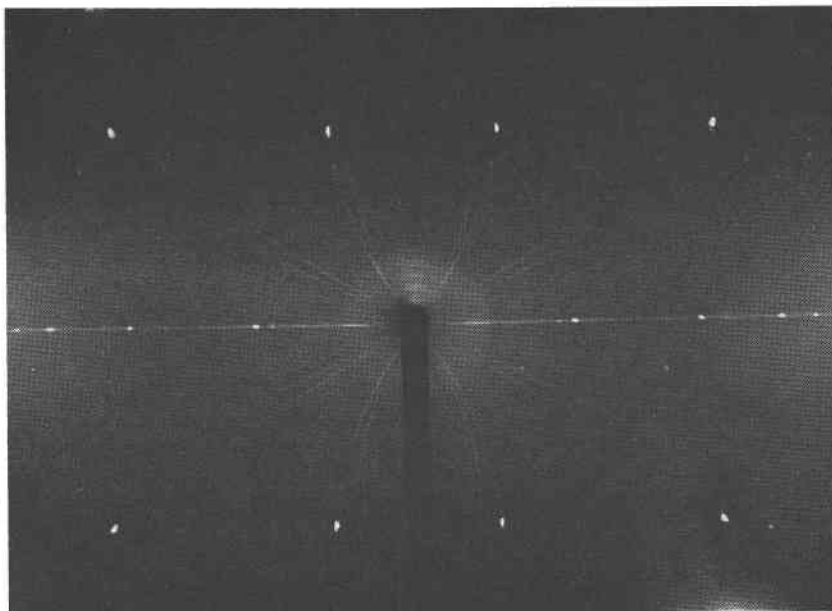


FIG. 4. Rotation pattern of natural diamond. FeK $\alpha$ , 12 hrs., [110] rotation.

Data pertinent to this discussion are summarized in Table 1. Ni and Co form carbon-containing, face-centered cubic, metal phases analogous to martensite,  $\gamma$ Fe. These phases are stable under the experimental conditions used, and the neutral radii of Ni and Co result in cubic cell dimensions essentially the same as that of diamond. Oriented inclusion within the crystallizing diamond structure is the expected result. The fact that the "satellite" phase is not a pure metal but contains carbon is demonstrated by the relatively high intensity of the (200) reflection (Lonsdale *et al.*, 1959).

Although Fe, with a neutral radius only slightly larger than Co, forms a face-centered cubic  $\gamma$  phase, martensite, of the proper cell dimension, this phase is not stable under the experimental conditions used. Instead a

body-centered cubic  $\delta\text{Fe}$ , having no fit with the diamond structure, is stable. Mn, with a neutral radius of 1.37 Å, forms a considerably larger  $\gamma$  phase, in addition to which the form stable at high temperature is again body-centered cubic  $\delta\text{Mn}$ . Thus no "satellite" phase forms when diamond is grown from Mn or Fe.

*Carbides:* Under the conditions of the experiments, carbides are to be expected as normal reaction products. Except with the pure metals Ni, Co, and Pt, such phases were observed. These ranged from single-crystal  $\text{Cr}_3\text{C}_2$  in the case of inconel and Cr to somewhat more complex carbides with Fe and Mn. The  $\text{Cr}_3\text{C}_2$  occurred as black needles at the graphite-metal interfaces (where all carbides were found) and could easily be leached from the matrix. Single-crystal rotation and Weissenberg patterns established the phase. The carbide observed in the case of Ta was

TABLE 1. DATA ON FACE-CENTERED CUBIC " $\gamma$ " METAL PHASES

Element	Neutral Radius (Å)	Cell Edge (Å)	
		"Satellite"	$\gamma$ Phase
Ni	1.24	3.539	
Co	1.25	3.567	
Fe	1.26		3.591
Mn	1.37		3.863

Diamond cell edge = 3.567 Å.

always TaC. With Fe, the common carbides  $\text{Fe}_2\text{C}$  and  $\text{Fe}_3\text{C}$  were sought, but only the latter has positively been found. Another common Fe carbide in the reaction products examined was a phase whose  $x$ -ray powder pattern contained all the lines of the 1:1 compound "FeC" described by Eckstrom and Adcock (1950). Judging from the literature, this phase appears to be somewhat evasive, but under the experimental conditions used in the present study, the pattern was obtained frequently. Mn-containing experiments yielded isostructural "MnC," concerning which the authors were unable to find a reference in the crystallographic literature. With both Fe and Mn,  $x$ -ray powder patterns of the 1:1 carbide showed lines not listed by Eckstrom and Adcock. These have features in common with the pattern of  $\text{Cr}_7\text{C}_3$  due to Westbrook (1961). An additional, remarkably well-crystallized carbide was  $\text{Mn}_3\text{C}$ , isostructural with cementite,  $\text{Fe}_3\text{C}$ .  $\text{Cr}_3\text{C}_2$  was the only carbide of Cr positively identified. All carbides with the exception of  $\text{Cr}_3\text{C}_2$  occurred in polycrystalline, fine-grained form. A discussion of the relation of carbides to the diamond

growth process is presented in the accompanying paper (Giardini and Tydings, 1962).

#### ALTERATION ZONE REACTION PRODUCTS

*Coesite-kyanite:* It has been shown earlier (Giardini *et al.*, 1961) that the pyrophyllite alteration zone (C, Fig. 1) invariably contains the phases kyanite and coesite. In experiments using Ni, inconel, Mn, Pt and Ta, the alteration zone was perfectly normal, with no coloring. Portions of the coesite-kyanite area were found to be blue with Co, brown with Fe, and green with Cr. Analysis of the colored materials by emission spectroscopy established that the coloring agent in each case was the respective end-plug metal. Colored phases were established by experiments involving treatment with HF, observation with the petrographic microscope, and *x*-ray powder diffraction of beneficiated material. Results showed that Fe and Cr tinted kyanite, whereas Co seemed to color the silica phase.

*Garnet:* In two specific cases, one involving Pt and the other Cr, the pyrophyllite alteration zone yielded minute, widely-scattered, light-brown crystals. Powder patterns and single-crystal rotation and Weissenberg patterns revealed a garnet phase having a cell dimension of 11.537 Å. Emission spectroscopy showed the presence of iron, indicating that the garnet phase might be almandite. The latter was confirmed by comparison with observed (Berry, 1959) and calculated (Table 2) cell dimensions. The iron was traced to an impurity in the original pyrophyllite. Two-circle optical goniometry enabled the indexing of two forms, {110} and {112}. Having established the formation of almandite under the experimental conditions used, the phase was sought and found in reactions employing Fe end plugs. Furthermore, Mn-containing runs were examined for a garnet phase, and spessartite ( $a=11.62_8$  Å, Table 2) was identified.

A pink-purple phase, found at the alteration zone—metal end plug

TABLE 2. GARNET CELL DIMENSIONS

Phase	Cell Edge (Å)	
	Calc.	Obs.
$\text{Fe}_3\text{Al}_2(\text{SiO}_4)_3$ (almandite)	11.53 <sub>8</sub>	11.53 <sub>7</sub>
$\text{Mn}_3\text{Al}_2(\text{SiO}_4)_3$ (spessartite)	11.62 <sub>3</sub>	11.62 <sub>3</sub>
$\text{Co}_3\text{Al}_2(\text{SiO}_4)_3$	11.47 <sub>5</sub>	11.47 <sub>1</sub>
$\text{Ni}_3\text{Al}_2(\text{SiO}_4)_3$	11.42 <sub>6</sub>	—

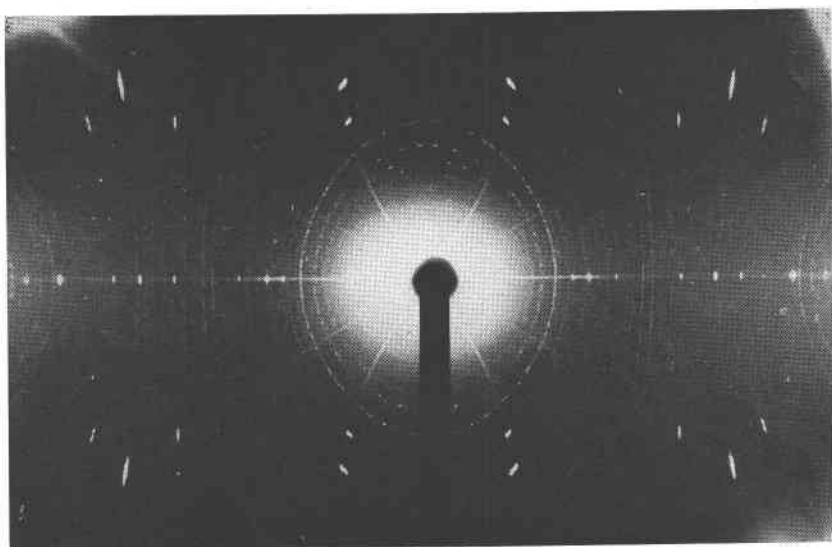


FIG. 5. Rotation pattern of Co-grown diamond, showing superimposed lines of intergrown Co garnet. FeK $\alpha$ , 12 hrs., [110] rotation. Crystal slightly misoriented.

interface in the case of Co, was shown to be a garnet by powder patterns. The position of the phase in the reaction chamber, together with its color, suggested a Co garnet, but the possibility of Ni (from the electrical contact discs) in the stoichiometry was considered. Spectrochemical analysis of the concentrated phase showed the presence of Co and the absence of Ni. As further evidence, cell dimensions were calculated, using the empirical equation for aluminum silicate garnets derived by Bertaut and Forrat (1957). With Co and Ni in dodecahedral (eight-fold) sites, the values shown in Table 2 were obtained. Agreement in the case of Co strengthens the argument in favor of the proposed stoichiometry. This appears to be the first successful introduction of substantial amounts of the relatively small Co<sup>2+</sup> cation into a garnet and is undoubtedly due to the effect of high pressure.

Almandite and Co garnet were occasionally intergrown with diamond crystals. Figure 5 is a [110] diamond rotation pattern showing superimposed lines of polycrystalline Co garnet. Such intergrowths facilitated the determination of cell dimensions, since diamond acted as an internal standard. It is interesting to note that garnet is a fairly common inclusion in natural diamond.

*Spinel:* In the one case of Ni, a light-blue phase, collected from the area common to the graphite charge, Ni end plugs, and pyrophyllite alteration



zone, proved to be the spinel  $\text{NiAl}_2\text{O}_4$ . A similar, minute phase noted with Co indicated the spinel  $\text{CoAl}_2\text{O}_4$ , but diffraction results were inconclusive.

*Miscellaneous:* Several experiments, involving various metal starting materials, showed a few unidentified high-spacing diffraction lines in samples taken from the pyrophyllite alteration zone. The spacings observed indicated the presence of one or more hydrous aluminum silicates, similar to dickite. Water can be derived from the original pyrophyllite.

#### SUMMARY AND CONCLUSION

A combination of x-ray diffraction, petrographic microscopy, emission spectroscopy and optical goniometry, as applied to specimen capsules subjected to high-pressure high-temperature conditions, has enabled the detection of two distinct modes of diamond formation and the identification of various carbides, garnets, spinels, etc., as secondary reaction products. The results indicate a promising future for the study of phase relations at very high pressures and high temperatures.

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