

carbon atoms diffuse through the cementite and precipitate from a preferred lattice plane, the lattice of cementite provides an excellent orientation for the epitaxial growth of graphite. Graphite was reported to grow perpendicular to the lattice plane of  $\text{Fe}_3\text{C}$  with its layer plane.<sup>28</sup> Cementite has an orthorhombic lattice with cell parameters  $a = 5.091 \text{ \AA}$ ,  $b = 6.743 \text{ \AA}$ ,  $c = 4.526 \text{ \AA}$ . Its b-axis is almost the same as the c axis of graphite ( $6.724 \text{ \AA}$ ). This is helpful for the crystallization of graphite. Catalytic crystallization in the metal dusting environment leads to coke with a much larger crystallite size and smaller interlayer planar distance than the carbons produced by other methods at similar temperature.<sup>11,18-20</sup>

The catalytic crystallization effect of iron was proven by Nakamizo et al.<sup>29</sup> and Kammereck et al.<sup>30</sup> They investigated the effect of iron on the crystallization of glassy carbon made from furfuryl alcohol. Only 3% addition of iron led to a dramatic decrease in the widths of the D and G bands and the D/G intensity ratio. The line widths of carbon with iron present annealed at  $600^\circ\text{C}$  were narrower than those of the carbon without iron annealed at  $2000^\circ\text{C}$ .<sup>29</sup> X-ray diffraction showed that addition of iron narrows the graphite [002] XRD peak dramatically.<sup>29,30</sup> These experiments showed that the crystallization rate of carbon is dramatically increased by the presence of iron or cementite catalyst.

### **Metal Dusting of Pure Metals**

Pure Fe and Ni specimens were examined over a range of temperatures and gas chemistry conditions to evaluate their susceptibility to metal dusting reactions and also to establish a baseline for comparison with the performance of Fe-base and Ni-base alloys, which are of interest for application in reformer environments.

Much of the earlier discussion has already treated carbon deposition in experiments conducted on pure Fe specimens exposed under various conditions. In addition to the analysis of the carbon deposit obtained from different runs, we also completed weight change measurements and detailed microstructural evaluation by electron-optical techniques, X-ray diffraction, and Raman spectroscopy on the Fe specimens. Following each exposure period, specimen weight change was determined after removal of adhering coke in an ultrasonic bath with acetone. Figure 24 shows the weight change data for pure Fe specimens in Runs 1 through 7, the experimental details for which are listed in Table 4. The data show that Fe is very susceptible to metal dusting attack and exhibits significant loss of metal in all the runs. The presence of 2 vol.%  $\text{H}_2\text{O}$  in the gas mixture (e.g., Gas 5 vs. Gas 4) may cause some delay in initiating metal dusting, especially based on data from 5-h exposures in Runs 7 and 6. However,  $\text{H}_2\text{O}$  at the 2% level has almost no effect at  $593^\circ\text{C}$  ( $1100^\circ\text{F}$ ) over the longer time period of 100 h (Runs 2 and 3). The wastage seems to be less at the higher temperature of  $704^\circ\text{C}$  ( $1300^\circ\text{F}$ ) compared with  $593^\circ\text{C}$  ( $1100^\circ\text{F}$ ), irrespective of the  $\text{H}_2\text{O}$  content of the gas.

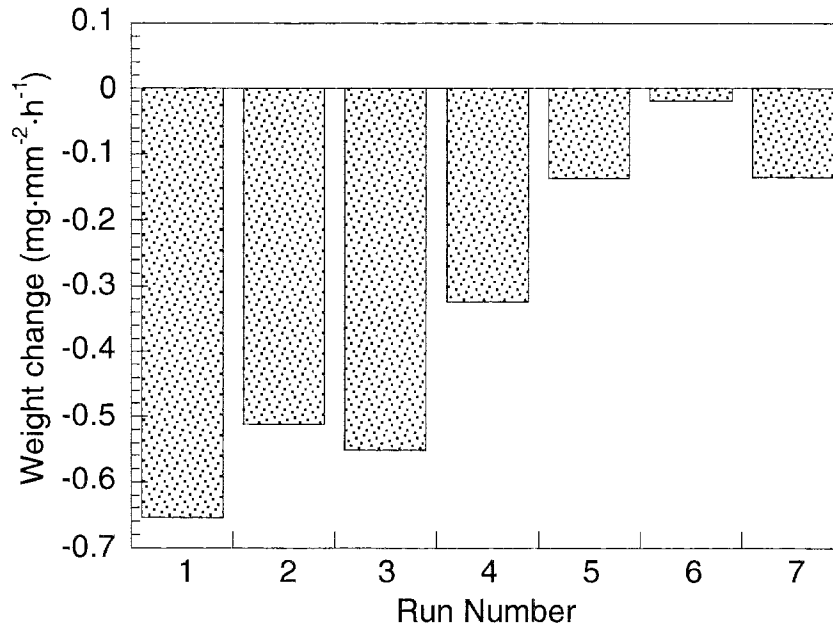


Fig. 24. Weight change data for pure Fe specimens exposed in Runs 1 through 7. Experimental details are listed in Tables 1, 2, and 4.

In our proposed catalytic crystallization process, carbon dissolves on the surface of the iron and crystallizes out in the bulk iron. Because the free energy of coke is probably higher than that of well-crystallized graphite, the saturating concentrations for coke and graphite will be different. High-free-energy coke should have a slightly higher saturating concentration than that of graphite ( $a_C=1$ ); if so, the saturating concentration of coke will be oversaturating for graphite. Therefore, poorly crystalline coke could dissolve in iron or cementite and move away as well-crystallized graphite. In this process, carbon transfers from the cementite surface and grows inward via the defects or grain boundary of cementite or iron. The accumulation of carbon in alloy causes the metal particles to disintegrate, as seen in Fig. 25.

Figure 26 shows a schematic of a process in which cementite particles separate into small particles as carbon particles accumulate at the defects. Such a transport process will continue until the cementite particles become too small to provide a template for carbon growth to 10-nm-size crystals (Table 5). The metal finally becomes nanometer-size dust in this process. X-ray diffraction shows that the average size of the cementite particles in the coke is  $\approx 27$  nm.

The metal dusting process for iron can be described as follows:

1. Carbon deposits on the iron surface, supersaturating Fe.
2. Cementite forms at the Fe surface; the volume expansion creates defects.
3. Carbon diffuses through cementite and precipitates at defects of cementite.

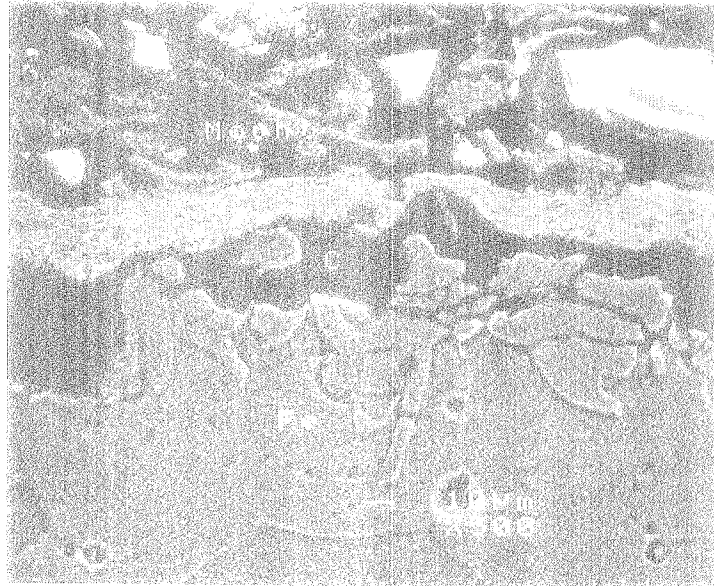


Fig. 25. Post test SEM micrograph of metallographic cross section of iron. Thinly bonded carbon layer found on iron surface after anisotropic etching. Iron particles are separated into small particles and move away from the iron surface.

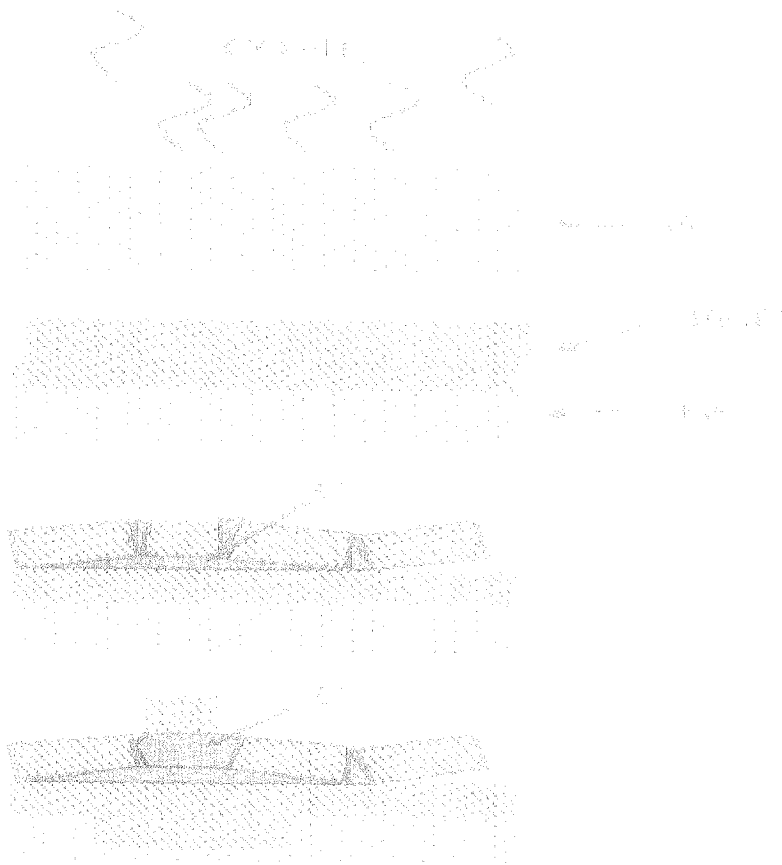


Fig. 26. Schematic of metal dusting process in the degradation of Fe.

4. Accumulation of carbon at the defects of cementite causes the cementite particles to separate into small particles and move away from metal.
5. Gas penetrates into the cracked area and continues further carbon deposition and the metal dusting process.

At high temperature, Fe may work directly as a catalyst in the crystallization of C since the iron lattice can also provide a good orientation for the growth of graphite. Carbon diffuses through Fe and precipitates at the defects. This precipitation also causes Fe particles to separate. Cementite forms when carbon diffuses into Fe. However, in the proposed mechanism, decomposition of  $\text{Fe}_3\text{C}$  is not a necessary condition to initiate metal dusting. Cementite acts as a medium for the diffusion and as a catalyst for crystallization of carbon. XRD shows that  $\text{Fe}_3\text{C}$  and carbon are the major phases in the products of metal dusting.

Pure Ni specimens were also exposed under different metal dusting environments in Runs 1 through 7. Figure 27 shows a comparison of Raman spectra (frequency range  $1000\text{-}2000\text{ cm}^{-1}$  and  $2000\text{-}4000\text{ cm}^{-1}$ ) for carbon adhered onto Ni surfaces after exposure in Runs 3-7. Specimens exposed at  $593^\circ\text{C}$  ( $1100^\circ\text{F}$ ) exhibited greater amounts of  $\text{sp}^3$ -type C-H bonds. Generally, the Ni surface was smooth before exposure, and polished surfaces can be seen in Fig. 28(a). The surface roughened after exposure, as can be seen in Fig. 28(b). A tightly adhering carbon layer was observed on the specimens, and neither ultrasonic cleaning nor acetone washing could remove the layer. To examine the specimen cross section, the carbon on the surface was separated from the carbon-containing mounting material by applying a silver paste to the sample surface before mounting. The thickness of the carbon layer was  $\approx 40\text{ }\mu\text{m}$ , but it was not uniform. Metallographic cross section showed that Ni separated and moved into the carbon layer (see Fig. 29), and a chemical analysis of the carbon/Ni mixture showed  $\approx 1\%$  Ni in the mixture.

The major phases in the metal dusting product are graphite and Ni metal (Fig. 30). The XRD [002] peak width of this carbon is broader than that of the well-crystallized graphite (Fig. 31), indicating that the crystallinity of carbon is poorer than that of graphite. The XRD [002] peak width of coke is even broader than the carbon present on the surface of Ni. However, it is much narrower than that of carbon black, which is made by thermal decomposition of gasoline vapor at  $704^\circ\text{C}$  (see Fig. 32). The peak position of carbon black moves to a small diffraction angle, which can be attributed to the degree of disorder, as discussed in an earlier section of the report.

The catalytic effect of Ni in the carbon recrystallization was studied by the following experiment. A mixture of glassy carbon and 10% nickel(II) bis(2,2,6,6-tetramethyl-3,5-heptanedionato) [ $\text{Ni}(\text{C}_{11}\text{H}_{19}\text{O}_2)_2$ ] was sealed in an evacuated quartz tube and slowly heated to  $1000^\circ\text{C}$ . The metalorganic precursor melted at  $225^\circ\text{C}$  and uniformly dispersed in the glassy carbon. At high temperature, the metalorganic compound

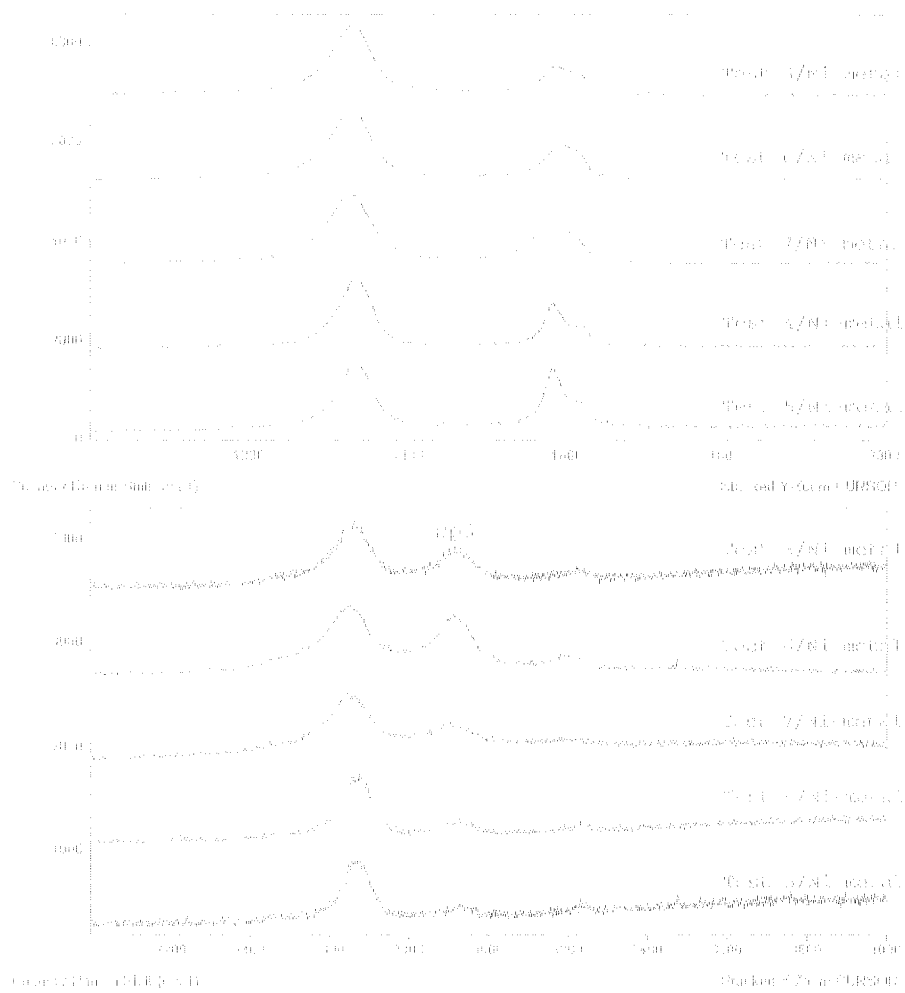


Fig. 27. XPS spectra for carbon adhered to Ni specimens from Runs 3-7. (Runs 3, 6, and 7 were conducted at 533°C (1000°F) whereas Runs 4 and 5 were conducted at 200°C (392°F).)

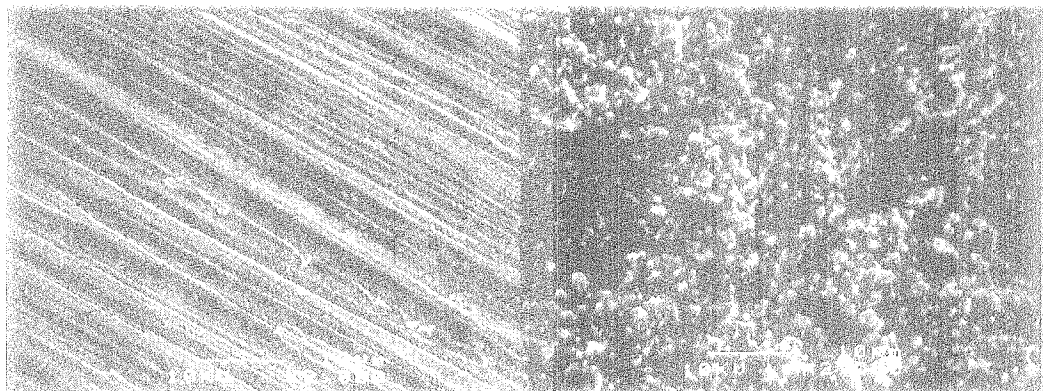


Fig. 28. SEM photomicrographs of Ni surfaces before and after exposure in a metal dusting experiment.

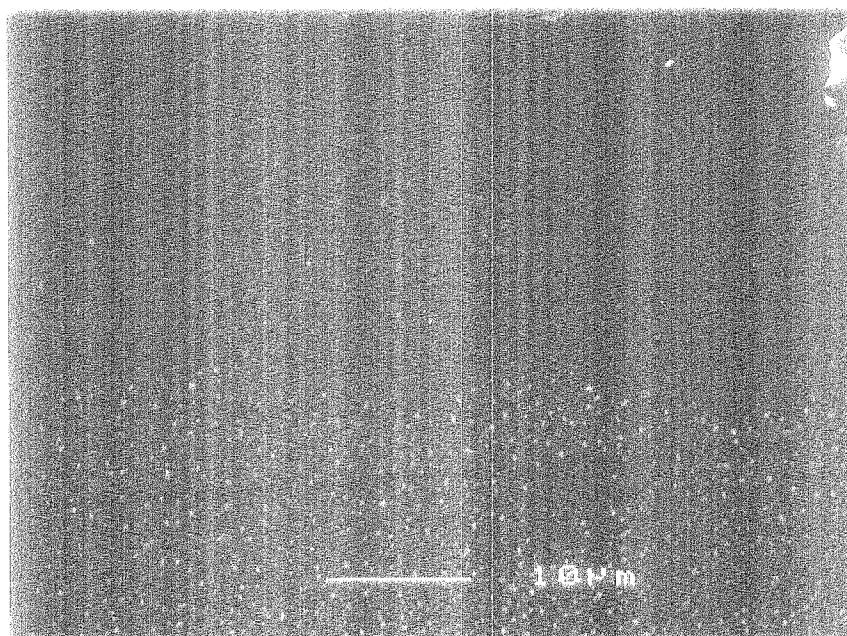


Fig. 29 SEM photomicrograph of cross section of Ni after testing. Tightly bound carbon layer found on the Ni surface, even after ultrasonic cleaning. Small particles of Ni separated and moved away from the surface.

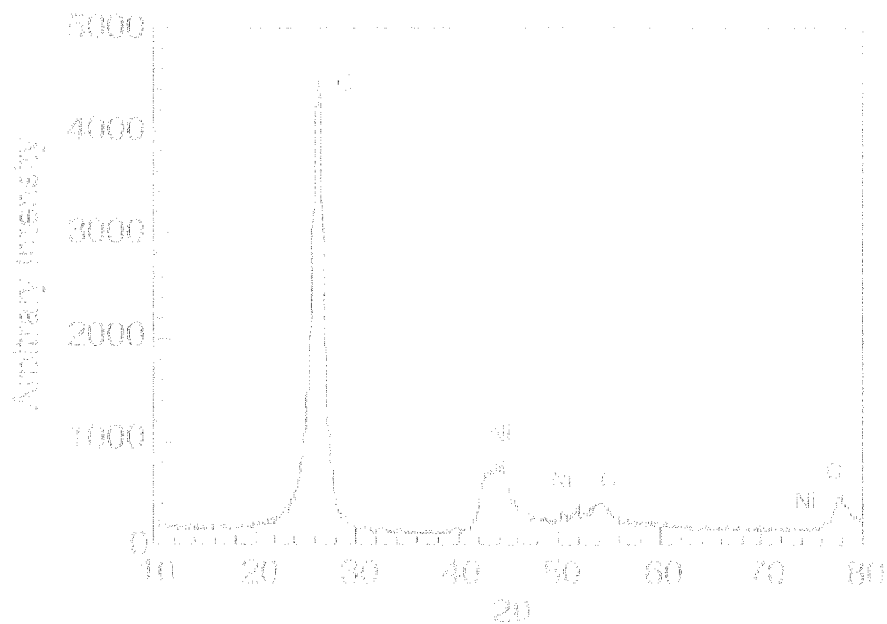


Fig. 30 Typical XRD pattern of the product of metal dusting; experiment involving Ni

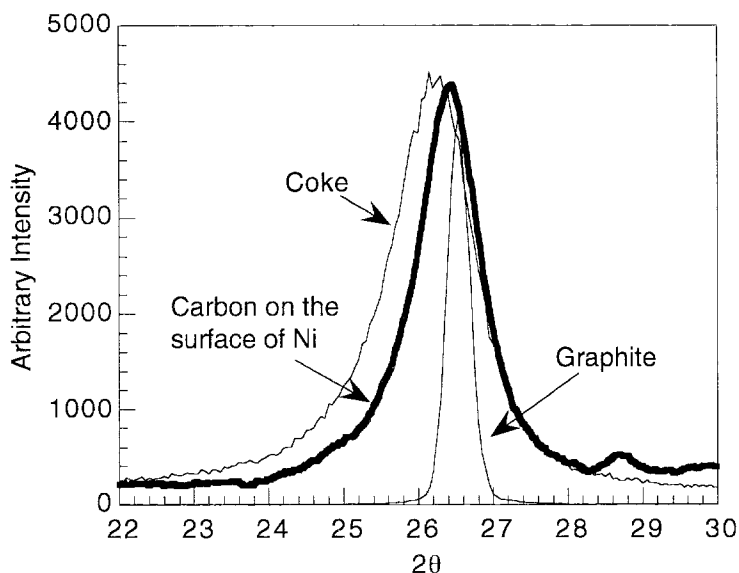


Fig. 31. XRD [002] diffraction peaks for graphite, coke, and carbon on the surface of Ni.

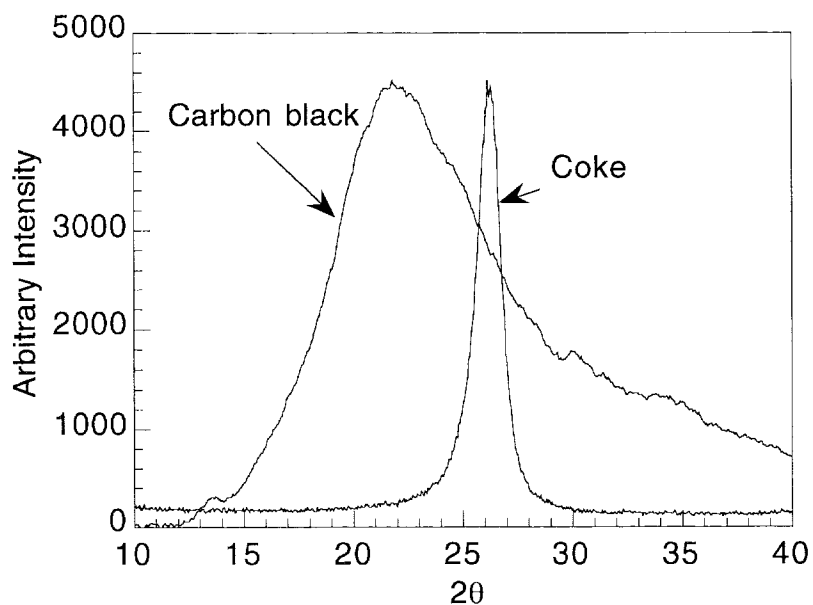


Fig. 32. XRD [002] diffraction peaks for carbon black and coke.

decomposed to nano-size nickel metal particles. These particles served as catalyst in the recrystallization of glassy carbon. Figure 33 shows that the carbon sample with 10% Ni has a much sharper peak than that of the carbon sample without Ni, even though they both were annealed at 1000°C for 100 h. These results clearly indicate that Ni can act as a catalyst to dramatically improve the crystallinity of carbon. Without the catalyst, carbon has less crystallinity at  $T < 1000^{\circ}\text{C}$  for the following reasons. First, the carbon layers in the graphite structure are easily disoriented because of the weak van der Waals forces between the layers. Second, recrystallization below 1000°C is hindered because the bond in the layers is too strong. The mechanism for metal