CATALYZED GRAPHITIZATION OF WOOD

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Abstract

Carbonization of cellulose and lignocellulose found in wood and similar plants has long been known to produce a non-graphitizable solid carbon. This paper discusses that carbonization process. It further demonstrates a process of catalytic graphitization of the non-graphitizable precursor. Heat treatment of wood at temperatures up to 2500°C is shown to result in an amorphous carbon as expected. Wood treated with metal oxides is shown to undergo graphitization at temperatures of 1500°C. The catalytic graphitization was found to have little influence over the elastic properties of the material as measured by acoustic velocity. However, x-ray diffraction suggests that there is a preferred orientation of the graphitic material within the carbonized wood. This study suggests the potential for altering the carbon structure of carbons derived from wood and opening up an array of new applications.

Key words: Graphitisation, Non-graphitic carbon, Charcoal

Introduction

Carbonization of wood and various plant materials has been practiced for thousands of years. Modern day practices have been driven by many objectives including the manufacture of activated carbons, feedstock for metallurgical processing, cooking fuel, and production of composite materials. It is clearly understood that these precursors are non-graphitizable, and the resulting char is typically amorphous with little preferred orientation of graphene layers.

It has long been known that the presence of certain metals or metallic compounds during heat treatment of a non-graphitic carbon can cause graphitization to occur at temperatures and pressures well below what is otherwise required. It has also been established that non-graphitizable carbons may be transformed into graphitic carbons by heat treatment with additions of metallic compounds.

Preservation of wood has been practiced for thousands of years. In 1838 the modern age of industrial timber preservation was born with the invention of pressure impregnation by Bethel [1]. This process involved full cell impregnation with creosote oil. In 1903 Dr. K.H. Wolman began developing salts for use as wood preservatives. Then in 1933 Dr. Sonti Kamesan invented the first copper, chrome, arsenate formulation (CCA). Bell Telephone had the first full scale commercial installation of CCA-treated poles during 1940-42. These proved so effective that the American Wood Preservers' Association (AWPA) included the Kamesan formulation as CCA-Type A (high Cr:low As) along with Boliden K33 as CCA-Type B (low Cr:high As) in their specifications. In the 1950's CCA-Type C was developed (by Hickson Corp.) as a median chromium:arsenic formulation. The three formulations of CCA contain different proportions of chromium trioxide (CrO_3), copper oxide (CuO), and arsenic pentoxide (As_2O_5). CCA-Type C (the formulations are also referred to as type I, type II, and type III) as covered by the U.S. Federal specification TT-W-550 and AWPA standard P5 should have a composition of 47 wt% CrO_3, 19 wt% CuO, and 34 wt% As_2O_5. For southern yellow pine AWPA standard C3 C18 requires CCA retention of 2.50 lbs/ft^3 (specified on an oxide basis) to protect against the marine borer Limnoria triunctata [2]. As specified in ASTM standard D 1760-86a retention of CCA for above ground use should be 0.25 lb/ft^3, and 0.40 lb/ft^3 when ground is contacted.

In the United States CCA treated lumber was extensively used until 2004 when it was phased out for most residential applications. The treated lumber still in service has been forecast to someday become a hazardous waste issue. In a study of methods to dispose of the waste wood, a series of tests to study thermal decomposition were conducted. The resulting studies demonstrating the transformation of wood to graphitic carbon is the topic of this paper.

Background

Mechanisms that have been proposed for catalyzed graphitization fall into four categories as considered by Noda [3]. These are; a) solution of carbon in metals or metallic compounds, and subsequent deposition or precipitation as graphite, b) formation and subsequent decomposition of a carbide, c) substitutional solid solution

of foreign elements in solid carbon inducing stress graphitization, and d) chemical reaction during carbonization resulting in structural change of resulting solid carbon.

Chemical reaction during carbonization in principle is not true catalyzed graphitization. It should be considered as a chemical modification of precursor polymer to alter decomposition and cross-linking mechanisms in a way as to promote a fluid mesophase. A thorough review of the literature found no work to support this mechanism. However, in 1966, Yokokawa et al. reported on work using cupric fluoride and cupric oxide for catalyzing the graphitization of non-graphitizable solid carbon precursors [4]. When the copper compounds were added to pitches no effects were found. However, when added to resins which normally give non-graphitizable carbons, a graphitic carbon was obtained after graphitization heat treatment. Intermediate compounds between the copper and carbonized resins were not identified but were suggested as being responsible for graphitization in some cases. In short, they suggested that graphitization only occurred if the structure of the solid carbon was suitable for interacting with the intermediate compound. They also found that the addition of the copper compounds to carbonized non-graphitizable materials could induce graphitization. It is likely that the metallic compounds acted through either the first or second mechanism mentioned above.

Pyrolitic graphite doped with boron (boron pyrolytic graphite, BPG) was found to increase in degree of graphitization by Kotlensky and others [5]. The effect was determined to be a maximum at 1 wt% boron levels by use of x-ray diffraction techniques. Boron substitution was thought to be either at trigonal sites or as an interstitial in the carbon lattice. Suggested complications in deducing mechanisms for a catalytic effect was the coincidence of maximum degree of graphitization with maximum and minimum of properties such as coefficient of thermal expansion, modulus, and thermal conductivity. These effects were thought to result from either the beginning of interstitial boron atoms or from the clustering of boron carbide.

The two most widely accepted mechanisms responsible for catalyzed graphitization are; a) a solution-precipitation of carbon from a metal or, b) an intermediate formation of a carbide which then precipitates carbon or decomposes leaving carbon. The driving force behind these mechanisms, as shown by Fitzer, is the difference in free energy between the non-graphitic and graphitic carbons [6]. Fitzer studied, by use of diffraction, microscopic and microprobe analysis techniques, a variety of solid carbons of varying degrees of order heat treated with either V, Ti, Zr, Ni, or Fe. He illustrated that the concentration of carbon in a carbide phase that is in equilibrium with a glass-like carbon should be higher than in equilibrium with graphite. The analysis showed how a melt can penetrate a micro-porous glass-like carbon via wetting caused by a tendency of disordered carbon to dissolve in the carbon saturated melt. The melt was supersaturated with respect to graphite so carbon is precipitated as well-ordered graphite. Also found was a lack of solubility of natural graphite (highly ordered) in a carbide melt.

In a study of palladium catalyzed graphitization Holstein outlines several criteria needed for acceleration of graphitization. It was proposed that a metal is not active as a catalyst if carbon has a low solubility in it and, the metal carbide is highly stable or, the metal doesn't wet the solid carbon [7]. For some metals which form carbides at high temperatures, graphite may form from the decomposition of the carbide via evaporation of the metal. Silicon carbide is an example of such metal carbide which decomposes forming graphite.

A number of investigators have studied catalytic effects of different metals and all come to the same conclusions regarding mechanisms involved [8-11]. When solution-precipitation is considered from a solid state metal it is presumed that at elevated temperature carbon has a relatively high solubility and precipitates out when solubility decreases with decreasing temperature. Liquid metals follow a similar scenario. Carbide phases form that decompose to the metal and to graphite. Reports of catalytic graphitization by nickel at temperatures below 600˚C have been given by Itoh and Sinclair [12]. They were able to detect phase transitions with differential scanning calorimetry and confirmed the phases and morphology by diffraction and microscopic techniques. Solution-precipitation was again the reported mechanism. This phenomenon is commonly observed in cast iron where it is possible to produce large graphite crystals from a supersaturated melt. In addition, oxides of both copper and chromium have been reported as catalysts for graphitization [4, 13].

In reviewing the literature further it is found that catalytic graphitization of solid carbons result in a material which is inhomogenous due to localized regions of graphitic carbon surrounded by non-graphitic carbon. When thin films are transformed the resulting material has somewhat less inhomogeneity owing to the small volume involved. Thus, it is apparent that production of monoliths of highly aligned, graphitic material cannot be attained by catalyst additives alone.

Methods and Results

Thermal analysis of wood and CCA pressure treated wood was performed using DTA/TGA. Commercially available southern yellow pine (CCA treated and untreated) was analyzed in nitrogen atmosphere to determine the decomposition mechanisms. The results indicated that decomposition of CCA treated wood proceeds through the

same stages as untreated wood. Considering the small quantity of CCA (0.4 lb/ft^3) it is possible that any minor alterations in wood decomposition mechanisms, or the presence of CCA decomposition, were undetectable by this method.

Elemental analysis by Energy Dispersive X-ray (EDX) technique of the Scanning Electron Microscope (SEM) was performed to determine whether any of the copper, chrome, or arsenic compounds remained in the carbonized treated wood. Analysis was performed on CCA treated yellow pine and the same carbonized to 600˚C, 800˚C, and 900˚C heat treatment temperatures (HTT). In all cases positive identification of chromium, copper, and arsenic was made. The results from the sample carbonized to 800˚C are presented in Fig. 1. The data shows clearly the retention of Cr, Cu, and As, as well as the presence of sulfur, potassium, and calcium (typical inorganics found in wood).

Testing was performed to characterize crystalline phases as a function of HTT in different samples of carbonized wood. X-ray diffraction (XRD) analysis of untreated carbonized wood indicated a low degree of atomic order in specimens heat treated to 2500˚C. Typical XRD results are shown in Fig. 2. Broad peaks from {002} reflections indicate non-graphitic carbons at all temperatures. Reflections from the {100} and {101} planes were broad and overlapped. These results were not surprising since lignocellulosics are well known for producing non-graphitizable carbons (even at HTT up to 3000˚C). However, a carbonized sample of CCA treated yellow pine gave a strong {002} reflection. This initiated a study of catalyzed graphitization with HTT.

Two precursors were selected for the heat treatment study. Commercially available CCA treated yellow pine (Pinus spp.) and Honduran mahogany (Swietenia spp.) as an untreated reference. Samples of both were carbonized at rates slow enough to avoid significant cracking then heat treated to either 900˚C, 1100˚C, 1300˚C, 1400˚C, or 1500˚C in an argon atmosphere. X-ray diffraction was then used to detect the onset of catalyzed graphitization. None of the prepared samples showed indications of three-dimensional long range order for graphite at 1400˚C or below. At 1500˚C the CCA treated sample gave a strong peak from the {002} reflection. This is shown in Fig. 3 where diffraction data from treated samples heat treated to 1400˚C and 1500˚C are plotted on the same graph. Catalyzed graphitization of the "non-graphitizable" carbonized treated wood is found to occur between 1400˚C and 1500˚C HTT.
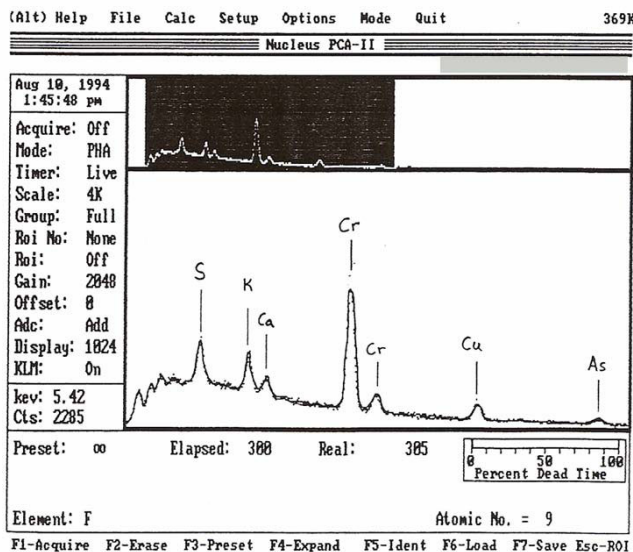
Figure 1. Elemental analysis (EDX) of carbonized CCA pressure treated yellow pine. Some Cr, Cu, and As is retained when the precursor is carbonized (HTT 800˚C).
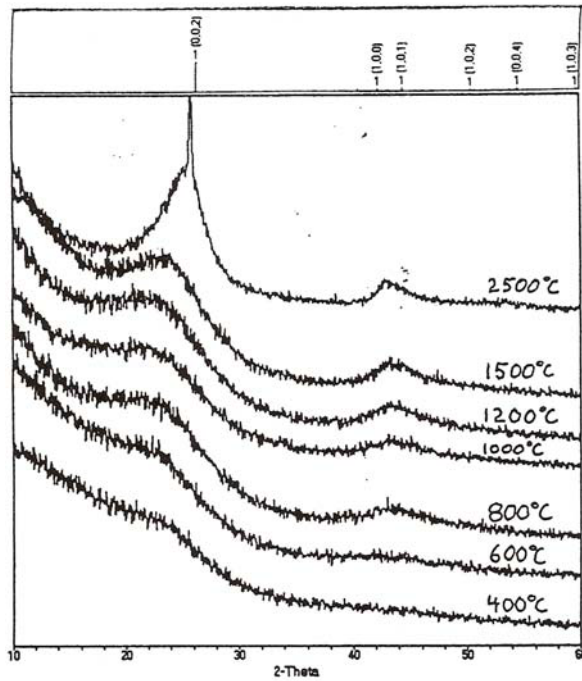
Figure 2. X-ray diffraction of wood carbonized to various temperatures.
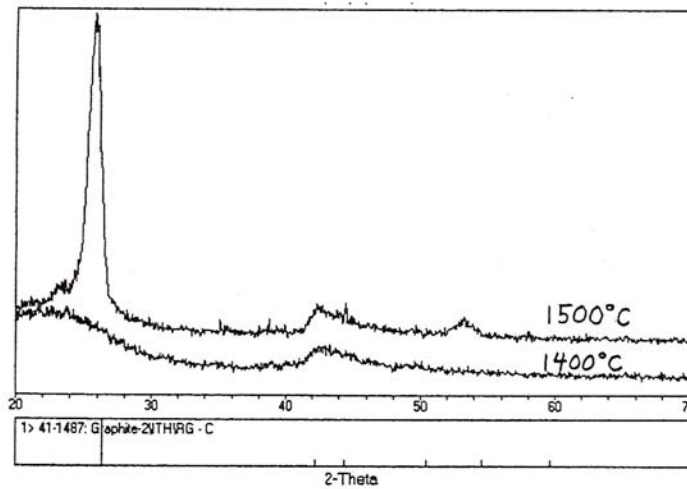
Figure 3. Catalyzed graphitization produced by CCA chemical modification of precursor wood. Graphitization occurs between 1400-1500˚C.

Further analysis of the catalyzed graphitization was attempted by performing thermal analysis on 600˚C carbonized treated wood. Analysis at temperatures up to 1550˚C gave inconclusive results. A slight endotherm at ≈1350˚C may have been the result of catalyzed crystallization but baseline values were too unstable to say with certainty. The particular mechanism responsible for forming graphite from the hard carbon was not investigated. It is likely that the preservative compounds which remained in the solid carbon catalyzed graphitization through a solution-precipitation mechanism either from metallic phases or metallic oxide phases. Oxides of both copper and chromium have been reported as catalysts for graphitization [4, 13].

The presence of a graphitic phase in the carbonized treated wood suggested the possibility of being able to alter the mechanical properties of monolithic carbonized wood via micro-structural modification. One specimen of CCA treated yellow pine heat treated to 1500˚C was tested to failure in compression. From this measure a

longitudinal stiffness of 1.23 Msi was determined. This compared closely to that found from carbonized poplar. Strength values were also similar to that of carbonized poplar and were higher than those found for the wood.

Ultrasonic velocity (at 1 MHz) measurements of CCA treated wood measured a compressional wave wavespeed similar to that found from untreated carbonized wood. At HTT of 1500˚C values of approximately 5000 m/s were found. This indicated no significant increase in elastic properties occurred from catalyzed graphitization. If a significant preferred orientation of graphite crystallites was present in the material, substantial changes in mechanical properties should have been found. The results, therefore, suggest little, if any, preferred orientation in the graphitized material.

Results from x-ray diffraction were not consistent with the observations from mechanical property testing. Monolithic specimens of graphitized CCA treated yellow pine were scanned with the source beam incident upon different principal faces. Only the tangential/axial (TA) face gave a peak for the {002} reflection of graphite. No similar reflection was observed on the other two faces (RT and RA). This preliminary investigation, unlike the mechanical test results, indicated a high degree of preferred orientation of the graphitic carbon. Further x-ray experiments are planned to establish the nature and extent of preferred orientation. In addition, high resolution transmission electron microscopy will be used to determine whether graphitic domains are continuous or inhomogenous in the graphitic carbon produced from CCA treated wood.

Conclusions

Heat treatment of wood at temperatures up to $2500^{o}C$ usually results in an amorphous carbon. Carbonization of wood can produce a graphitizable solid carbon when certain additives are present in the original wood. The CCA pressure treated lumber contains catalytic compounds that can influence the carbonization process and allow graphitization to occur at under 1500˚C. The metal oxides used in the preservative likely create the catalytic graphitization of the hard carbon. The catalytic graphitization was found to have little influence over the elastic properties of the material as measured by compression testing and acoustic velocity testing. In contrast, x-ray diffraction suggests that a preferred orientation of the graphitic material within the carbonized wood does exist.

References

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