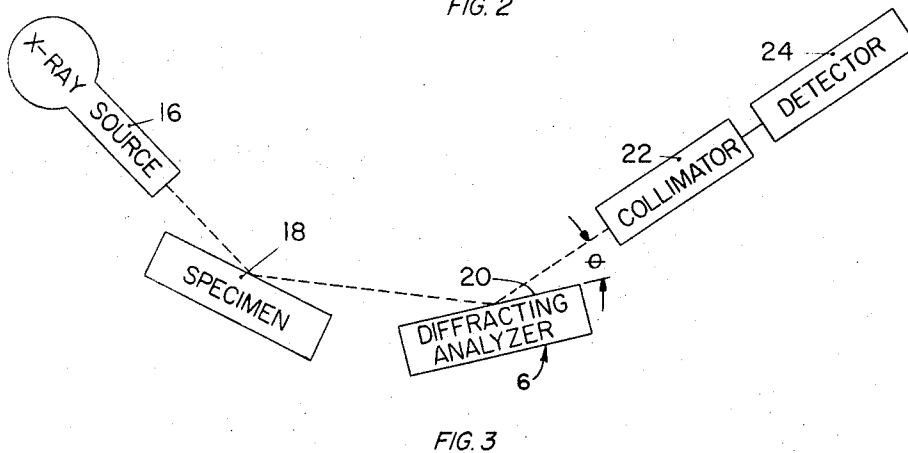
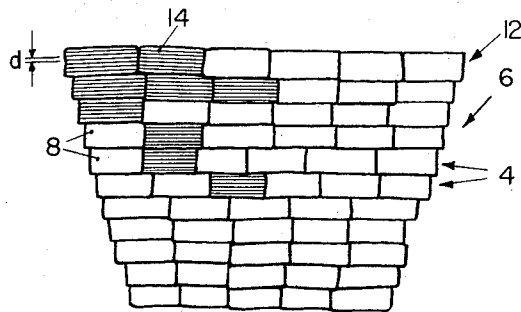
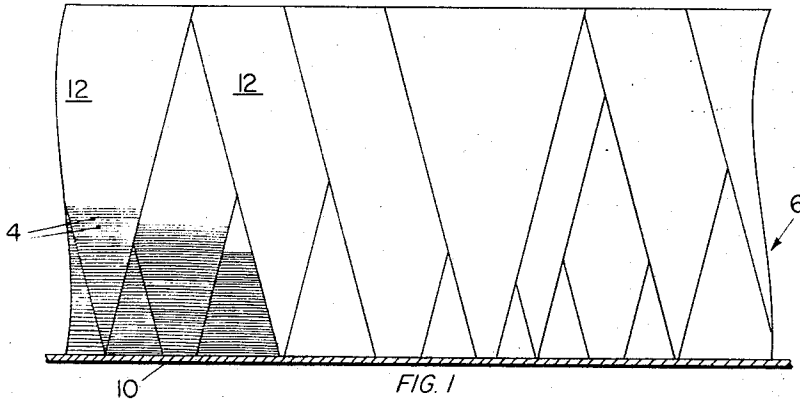


Jan. 28, 1969

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3,424,428

X-RAY SPECTROSCOPE ASSEMBLY HAVING AN ANALYZER
BLOCK COMPOSED OF ANNEALED PYROLYTIC GRAPHITE
ON AN OPTICALLY ACCURATE SURFACE
Filed Aug. 9, 1965



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1

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X-RAY SPECTROSCOPE ASSEMBLY HAVING AN ANALYZER BLOCK COMPOSED OF ANNEALED PYROLYTIC GRAPHITE ON AN OPTICALLY ACCURATE SURFACE

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Filed Aug. 9, 1965, Ser. No. 478,311

U.S. Cl. 250—51.5
Int. Cl. G01n 23/20

9 Claims

ABSTRACT OF THE DISCLOSURE

An X-ray spectroscopic system and process for analyzing selected material specimens wherein polycrystalline pyrolytic graphite is the X-ray analyzing means.

This invention relates to novel pyrolytic graphite; and particularly to a novel diffracting analyzer for use in X-ray spectroscopy, which is prepared therefrom.

In a conventional X-ray spectroscopy, the diffracting analyzer is an integral component of the system. This diffracting analyzer is a single crystal which is used to separate the various wavelengths emitted by the specimen. The better the resolution of such a crystal, the more easily the wavelengths from the specimen are separated into discrete lines characteristic of the elements therein.

One means of improving the resolution of the radiation is to increase the dispersing capability of the diffracting analyzer. The reason for this is that the angular separation of the incident wavelengths, and, hence the resolution, is governed by the equation

$$\frac{d\theta}{d\lambda} = \frac{n}{2d \cos \theta}$$

wherein n is an integer representing the order of reflection, λ is the wavelength of the incident rays, d is the spacing of the particular set of diffracting planes in the analyzing crystal (the interatomic planar spacing), and θ is the angle between the incident radiation and the diffracting planes of the diffracting analyzer. Hence, adjacent wavelengths may be detected farther apart and with better resolution as the interatomic planar spacing d is adjusted downwardly. Within limits, this spacing may be precisely controlled in the applicant's invention by adjusting the time and temperature of the annealing operation (which will presently be described).

Because of this requirement for resolution, the choice of diffracting analyzers is somewhat limited. Pure and perfect crystals of certain materials have been found to be of little value for this purpose, because many of them cause extinction of the impinging radiation.

Furthermore, it is essential that the diffracting analyzer be of good quality to produce sharp, symmetrical peaks representing characteristic wavelengths of the elements in the sample. Unless the crystal lattice or mosaic-block structure is properly oriented, the incident rays will be diffracted at deviant θ angles. Such defects could also decrease intensities, causing errors in the analysis. For these reasons, the analyzing crystals of the prior art have been limited to highly purified materials having the desired physical characteristics. These include quartz, and the crystals of the alkali metal halides such as lithium fluoride, sodium chloride, and potassium chloride.

2

Unfortunately, these materials are subject to certain limitations and disadvantages including (1) unavailability, (2) fragility, (3) poor diffracting efficiency, (4) poor capability of diffracting the longer wavelengths of incident radiation, (5) high cost and the difficulty of manufacture, (6) lack of replicability, and (7) characteristic wavelengths of their own that either interfere with wavelengths of the sample or contribute to high background or noise to the analysis.

For instance, synthetic crystals are tedious to prepare and require a high degree of skill to fabricate them. Nearly all of the currently-used analyzing crystals, whether natural or synthetic, are fragile and can be irreparably damaged when dropped or bumped. A narrow spectrum is also a problem. For instance, a typical analyzer, ammonium di-hydrogen phosphate, while useful for diffracting the characteristic wavelengths of lower-atomic-weight elements, is inefficient in detecting elements having shorter wavelengths. On the other hand, crystals of lithium fluoride or topaz, while useful in detecting elements having higher atomic weights, are comparatively inefficient in the detection of lighter-weight elements. Some of the commonly-used crystals are inefficient diffractors of X-rays. Gypsum, germanium, and sodium chloride frequently interfere with radiation from the specimens being analyzed by producing high characteristic background that may mask analysis of elements in the specimen. This may occur when the specimen contains elements that may produce wavelengths similar to those produced by elements in the crystal itself, or when the specimen contains elements whose radiation is capable of exciting elements in the crystal. Naturally-occurring crystalline products such as diamond, aluminum, and graphite frequently have different diffraction characteristics from crystal to crystal, and do not normally occur in the sizes and shapes satisfactory for spectroscopic use. Also, naturally-occurring crystals having properties satisfactory for this use are usually very expensive.

Because of the many shortcomings of the diffracting analyzers of the prior art, there exists a real need for an inexpensive diffracting analyzer of rugged construction which would diffract X-rays from elements of both low and high atomic weights relatively effectively. Other desirable attributes would be that the diffracting analyzer be made of elements having sufficiently-long characteristic wavelengths that would neither interfere with elements in the specimen nor contribute to background or noise, together with reproducible and identical diffracting characteristics, ease of manufacture and efficiency as a diffracter of radiation.

The above highly desirable characteristics heretofore unavailable in a single diffracting analyzer, are obtained, surprisingly enough, by the use of a new polycrystalline, pyrolytic graphite having unusual physical and dispersion properties. The precursor to this novel dispersing material is a pyrolytic graphite which is itself somewhat unique in that it is produced by unusually high temperature decomposition of carbonaceous materials upon an inert, thermally-stable, optically-accurate substrate. The term "optically-accurate," for the purpose of this application, will be taken to mean that degree of accuracy in the substrate surface that will produce optimum diffracting characteristics in the diffracting analyzer. As will become apparent later in this description, this involves several variables such as percentage of crystallites oriented within a

certain angle with respect to one another, a dust-free substrate surface, etc. In practice it has been found that the practical limit of permissible roughness and waviness represented by this term is of the order of 10 mils, and preferably two mils.

It is an object of this invention to provide a novel material suitable for use as a diffracting analyzer for X-ray spectroscopy.

It is a further object of this invention to provide a novel theretofore unavailable, inexpensive, polycrystalline pyrolytic graphite having an unusual combination of physical and optical properties. This material is useful for the above and other purposes, from readily available starting materials.

Another object of this invention is the preparation of the above polycrystalline graphite diffracting analyzer, highly resistant to cracking and breakage and capable of analyzing elements of both high and low atomic weights.

An additional object of this invention is the development of a novel preparative process useful in the preparation of the pyrolytic graphite from which the diffracting analyzer may be made, together with related uses of this novel graphite.

Further objects of the invention will become apparent to those skilled in the art after a further perusal of this application and the accompanying drawings.

FIGURE 1 is a cross section, schematic representation of the structure of the novel pyrolytic graphite diffracting analyzer of this invention.

FIGURE 2 is an enlarged portion of FIGURE 1.

FIGURE 3 is a schematic representation of a typical X-ray spectroscopy assembly employing the novel pyrolytic dispersion means of this invention.

In practice, a thermally stable, optically accurate and inert substrate is heated to at least 2500° C. and maintained at atmospheric pressure or at slightly less than atmospheric pressure in an environment of carbonaceous gas and in close proximity to the gas. The substrate is so positioned within the heating chamber that the decomposition of the carbonaceous gas which occurs at these temperatures takes place uniformly and evenly upon the substrate. Under these conditions of near atmospheric pressure and high temperatures, the pyrolytic graphite formed and deposited has unusually high density and rather low interatomic planar spacing d . The slow deposition rate requires lengthy heating times (over 12 to 24 hours) to obtain a diffracting analyzer having significant depth. After the desired amount of deposition has taken place (mils to hundreds of mils) the carbonaceous gas environment is withdrawn and the pyrolytic graphite is annealed by heating at a substantially higher temperature until its density increases to a maximum and the inter-layer distance decreases to its minimum value.

In the preferred practice, natural gas is passed through a sealed chamber under about ½ atmosphere pressure over an optically accurate, flat, pyrolytic graphite substrate heated preferably to over 2500° C.; a temperature much higher than that required to convert the natural gas quantitatively into pyrolytic graphite requiring no special diffracting or other physical properties. This heating of the substrate over 2500° C. is continued for an extended period of time until the desired thickness of graphite having a density of about 2.15 to 2.25 grams per cc. and a (002) d spacing of from about 3.37 to 3.45 is produced. At this stage while the pyrolytic graphite coating is of the desired thickness, the graphite does not have satisfactory physical and diffracting properties for use as a diffracting analyzer. In order to convert the coating to a suitable diffracting analyzer, further treatment is necessary. To improve the diffracting properties of the pyrolytic graphite to the required extent an annealing step is essential. This annealing is accomplished in the absence of the carbonaceous gas by raising the temperature to at least 3000° C. and maintaining the temperature at this

level for a minimum of two hours. The treated pyrolytic graphite is then removed, cooled, and machined to the desired shape and dimensions.

As illustrated by FIGURES 1 and 2 the general structure of the invention is an X-ray diffraction analyzer 6 of annealed pyrolytic graphite comprising laminations or layers 4 of flat crystallites 8 having diameters ranging in size from about several hundreds to several thousand angstroms oriented in general conformity to the surface of a substratum 10, and are arranged in growth cones 12 as the deposited graphite builds up on the substratum 10. The crystallites 8 are imperfect carbon crystals having general crystal-lattice structures arranged in parallel strata as represented by the parallel lines 14, separated by an interatomic planar distance d .

Low temperature (1600°–2500° C.) pyrolytic deposition of graphite is old. However, the art teaches deposition at very low pressures and for very short periods of time. Further, the pyrolytic graphite produced by this "low temperature quick process" produces a graphite product which is unsatisfactory for spectroscopic applications. Presumably these poor characteristics are caused by the lack of preferred orientation of the crystallites, which in turn is related to low density and large interatomic planar spacing d possessed by this material.

In addition and for reasons not presently clear, the un-annealed pyrolytic graphite derived from the processes of the prior art have crystallites of relatively small diameters which are not aligned substantially parallel to one another. In contrast the annealed pyrolytic graphic product of the applicant's high temperature, slow process, during which the deposition accumulates on the optically accurate surface of a substrate, has crystallites of much larger diameters and which are more or less laminated and lie substantially parallel to one another.

The following discussion of reaction conditions will set forth more clearly the advance over the prior art that is represented by the present invention.

The preferred temperature range for deposition is from at least 2500° C. to about 3000° C., although temperatures somewhat lower can be used in some instances. The range of 2500° to 3000° C. is effective for deposition of graphite for the purposes of this invention.

The pressure utilized during deposition is preferably about 380 mm. of mercury (½ atmosphere) but can range between about 380 to 760 mm. of mercury (atmospheric pressure).

The critical annealing step which, together with deposition on an optically-accurate substrate, is required to obtain an acceptable diffracting analyzer is conducted in the absence of a carbonaceous gas, at much higher temperatures ranging from about 3000° to 4000° C. or higher. The upper limit is primarily that of the heating capability of the furnace. Pyrolytic graphite having good diffracting properties is produced by annealing the graphite obtained in the deposition step from about 3000° C. to about 3600° C., and this represents the preferred annealing temperature range.

When the annealed pyrolytic graphite is used as a diffracting analyzer or for other similar use, the orientation of the crystallites is critical. Since this orientation is strongly influenced by the surface of the substratum it has been found that the practical surface variations between highs and lows is of the order of 2 to 10 mils, ideally no more than about 2 mils is preferred.

The simplest arrangement of a commonly used spectroscopy apparatus which employs diffracting analyzer 6 of this invention is illustrated in FIGURE 3. A source 16 of primary X-rays directs X-rays to specimen 18 to be analyzed. Fluorescent rays from the specimen 18 impinge upon the annealed pyrolytic graphite surface 20 of diffracting analyzer 6 of this invention and are directed by a collimator 22 to a detection device 24. The radiation source 16, the collimator 22, and detector 24 are all available commercially in a variety of shapes and forms both

for special and general purposes. Clearly the arrangement of components shown is only illustrative and can be varied considerably.

Depending primarily upon the shape of substratum 10, any of the commonly used configurations of diffracting crystals can be used. For example, a flat substratum will result in the preparation of a flat diffracting analyzer, a curved substratum will produce a curved diffracting analyzer, since layers 4 of pyrolytic graphite crystallites 8 conform to the curvature of substratum 10. A further embodiment of diffracting analyzer 6 of the present invention may be made by cutting the pyrolytic deposition at right angles to, or in a direction nonparallel to, deposition layers 4. This will result in a transmission type of diffracting analyzer 6, wherein X-rays from specimen 18 are diffracted through the analyzer 6.

To illustrate the process aspects of this invention, the following embodiment is submitted.

Natural gas is passed through a sealed deposition apparatus comparable to that disclosed by Diefendorf in U.S. Patent No. 3,138,435 over an optically-accurate, graphite substratum such as substratum 10 heated above 2500° C. The pressure initially is 380 mm. of mercury. After approximately 50 hours, the disposition of pyrolytic graphite on the substratum forms a coating approximately ¼ inch thick. The interatomic planar spacing d is approximately 3.43 angstroms before annealing. After withdrawing the coated substrate from the reaction chamber, the deposition of graphite is annealed at 3000° C. for four hours. This may be done either in situ, or the deposition may be removed from the substratum by machining. The coated article is then removed from the chamber, cooled, and machined to yield an X-ray diffracting analyzer. After annealing, the graphite density had increased to 2.25 g./cc. and the interatomic planar spacing d had decreased to 3.356 angstroms. Using the diffracting analyzer thus formed as analyzer 6 in the arrangement shown in FIGURE 3, a known sample or specimen 18 containing phosphorous and iron is analyzed. Good resolution of the wavelengths of both light-weight and heavy elements is obtained. In contrast, pyrolytic graphite produced following the directions of Example 1 of 3,138,434 without subsequent annealing, and without the graphite's having been deposited upon an optically accurate substratum surface, was found to be unsatisfactory as a diffracting analyzer for use in X-ray spectroscopy.

In a related embodiment of the invention, the above procedure is repeated with the exception that substratum 10 is heated to a temperature of above 1300° C. during the deposition step. The resulting product is of similar quality. In another related embodiment, a curved, optically-accurate substratum 10 is inserted into the apparatus cited above. The initial pressure is 380 mm. of mercury and again natural gas is used as the source of carbon. The graphite deposition proceeds at above 2500° C. for a period of 38 hours or until the desired thickness of graphite is obtained. At the end of this time, the now coated substratum 10 is removed and inserted into an annealing furnace maintained at a temperature above that required for deposition of the graphite. The annealing is continued for four hours. The coated article is then removed, cooled, and machined as before. Again a diffracting analyzer of good quality is obtained.

In still a further embodiment, the above procedure is repeated with the exception that the annealing step is conducted for a shorter period of time and at a pressure above two atmospheres. A diffracting analyzer having good dispersing characteristics is obtained.

This invention is advantageous in both its article of manufacture and its process aspects.

In the former instance, the specially annealed pyrolytic graphite of this invention is eminently suitable as a diffracting analyzer or for other purposes requiring the peculiar characteristics of the treated material. Unlike the pyrolytic graphite of the prior art, which is formed at relatively low

temperatures and short process times (or the graphite deposition of this invention in its unannealed form and without having been deposited on an optically accurate substrate as is described herein) the annealed diffracting analyzers of this invention are valuable dispersion means in X-ray spectroscopy. The material is especially suitable since it offers suitable diffraction properties for wavelengths of both low and high atomic weight elements. In addition, the diffracting analyzers so prepared are rugged and resistant to fracture or breakage, can be easily machined, and can diffract wavelengths of a number of elements generally.

In its process aspects, the invention yields a unique pyrolytic graphite which in some instances is far superior to the prior art materials for the purposes of this invention. Conventional heat treating and annealing furnaces can be employed. The carbonaceous gas used can vary considerably. In addition to natural gas and hydrogen, other hydrocarbons including methane, propane, acetylene, benzene, etc. can be used as well as halogenated hydrocarbons such as trichloroethylene, carbon tetrachloride and the like.

It is surprising that pyrolytic graphite could be used as a dispersion means in an X-ray spectroscopy. There is nothing in the prior literature that would suggest such use. In fact pyrolytic graphite, as prepared in the prior art, is indeed unsuitable for such use. However, when it has been prepared according to the processes described herein, including the steps of depositing the graphite on an optically accurate surface and of annealing this deposition at high temperatures, a unique product results which satisfies a long felt need and is very valuable in the art of X-ray spectroscopy. The teaching of 3,138,434 (column 3, lines 33-39) is that annealing of pyrolytic graphite produces a material having poorer properties than the unannealed graphite.

The particular substrate utilized can also vary considerably so long as materials used are thermally stable at the temperatures necessary for annealing the graphite deposition. Also the pyrolytic layer can be built up to any desired thickness and the substrate can be removed by machining.

As can be seen by the several embodiments and broad disclosure, numerous modifications and changes can be made without departing from the inventive concept. The metes and bounds of this invention are best described by the claims which follow.

What is claimed is:

1. In an X-ray spectroscopy assembly of an X-ray source, a diffracting analyzer, a collimator, and a detector, the improvement comprising;

50 said diffracting analyzer constructed of annealed pyrolytic graphite deposited in laminated crystallite layers substantially parallel to each other on an optically accurate graphite substratum surface.

2. In an X-ray spectroscopy assembly of an X-ray source, a diffracting analyzer, a collimator, and a detector, the improvement comprising an X-ray analyzer block, said analyzer block having at least one optically accurate surface, and comprising laminated layers of crystallites of annealed pyrolytic graphite thermally deposited on said surface said layers being oriented substantially parallel to each other, and

said annealed pyrolytic graphite having a density of from about 2.25 to 2.30 g./cc. and interatomic planar distances of about 3.350 to 3.400 angstrom units.

3. The X-ray spectroscopy assembly of claim 2 wherein the pyrolytic graphite layers are essentially curved.

4. The X-ray spectroscopy assembly of claim 2 wherein the pyrolytic graphite layers are essentially planar.

5. The X-ray spectroscopy assembly of claim 2 wherein said X-ray analyzer block is of the transmission type, wherein the surface for incident radiation, as well as the surface opposite thereto, is nonparallel to said laminated layers.

6. In the process for analysing material specimens by X-ray spectroscopy wherein X-ray are impinged upon the

7

surface of said specimens to effect emission of radiation therefrom, the improvement comprising the step of analysing said radiating specimen by a diffraction analyzer made of annealed pyrolytic graphite supported on an optically accurate, thermally stable substrate of graphite.

7. The process of claim 6 wherein the pyrolytic graphite is a crystallite structure oriented in substantially parallel laminations.

8. The process of claim 7 wherein the laminations are essentially planar.

9. The process of claim 7 wherein the laminations are curved.

8

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U.S. Cl. X.R.

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