

Graphite-halogens as temperature calibration standards for transmission electron microscopy^{a)}

D. D. L. Chung

Department of Metallurgy and Materials Science and Department of Electrical Engineering, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213

(Received 22 February 1979; accepted for publication 20 August 1979)

Graphite-halogen (Br_2 , ICl) residue compounds have been found to be convenient temperature calibration standards for transmission electron microscopy in the medium temperature range. Due to the order-disorder transformation associated with the intralayer intercalate ordering in these intercalation compounds, the observation of the disappearance of the superlattice diffraction spots as the sample temperature is raised serves to calibrate the temperature. The transformation occurs at $100 \pm 1^\circ\text{C}$ in graphite- Br_2 and $41 \pm 1^\circ\text{C}$ in graphite- ICl . The simplicity of specimen preparation gives added attraction to the use of graphite-halogens as temperature calibration standards.

PACS numbers: 07.80. + x

INTRODUCTION

Transmission electron microscopy is a widely used experimental technique in science and engineering. Because the structure and properties of materials frequently vary with temperature, electron microscopy is used not only at room temperature, but at temperatures below and above room temperature as well. High and low temperature electron microscopy can be carried out by using heating and cooling sample holders, which are supplied by the microscope manufacturers. Although these sample holders provide thermocouples for temperature measurement, the distance of the sample from the thermocouple and the heating effect of the electron beam on the sample¹ make the temperature measurement quite poor. The accuracy with the use of the thermocouple to obtain the sample temperature is at best $\pm 10^\circ\text{C}$. In order to achieve a higher degree of accuracy, temperature calibration must be performed by using a standard sample that exhibits a phase transformation at an accurately known temperature. However, to protect the vacuum in the electron microscope, the phase transformation should be a solid-state transformation. Because of the scarcity of suitable solid-state transformations at low and medium temperatures, temperature calibration at these temperatures has been a problem. This paper describes the use of graphite-halogens as medium temperature calibration standards. These materials exhibit solid-state transformations at temperatures known with an accuracy of $\pm 1^\circ\text{K}$. Moreover, they can be conveniently prepared and made sufficiently thin for transmission electron microscopy.

I. BACKGROUND ON MATERIALS

Graphite-halogens belong to a class of layer compounds known as graphite intercalation compounds.²⁻⁶ Graphite intercalation compounds contain the intercalate (foreign species) in interstitial layer planes of the graphite crystal such that the planar layer structure of the parent graphite is retained. These compounds exhibit an order-

disorder transformation associated with the superlattice ordering of the positions of the intercalate ions, atoms, or molecules within an intercalate layer. The transformation can be observed by noting the disappearance of the superlattice diffraction spots on the (001) reciprocal lattice plane as the sample is heated. The electron diffraction patterns of pristine graphite, graphite- Br_2 , and graphite- ICl at room temperature are shown in Fig. 1. For graphite- Br_2 and graphite- ICl , in addition to the hexagonal pattern of diffraction spots as for pristine graphite, there are superlattice diffraction spots; the superlattice diffraction patterns are different for different intercalates.

The order-disorder transformations in the graphite-halogens were first observed by the author by using the electron diffraction technique,⁷ which yielded an accuracy of $\pm 10^\circ\text{C}$ in the determination of the transformation temperature. To obtain a more accurate determination differential scanning calorimetry (DSC) was used.⁸ The transformation temperature was thus found to be $100 \pm 1^\circ\text{C}$ for graphite- Br_2 and $41 \pm 1^\circ\text{C}$ for graphite- ICl .

II. PREPARATION OF MATERIALS

One of the advantages in the use of graphite-halogens as temperature calibration standards is the simplicity in the preparation of electron transparent samples. This section describes first the preparation of the bulk material and second the method of obtaining electron transparent samples from the bulk material.

Graphite- Br_2 and graphite- ICl can be prepared by exposing pristine graphite (preferentially pyrolytic graphite) to Br_2 and ICl vapor, respectively, in air at room temperature for several days. This results in a lamellar compound which contains the maximum amount of intercalate. For graphite- Br_2 , the saturated lamellar compound has a chemical formula of C_{16}Br_2 ,³ which corresponds to an 83% increase in weight from the weight of the parent pristine graphite. For graphite- ICl , the

saturated lamellar compound has a chemical formula of $C_{8.5}ICl$,^{9,10} which corresponds to a 159% increase in weight from the weight of the parent pristine graphite. Although a saturated lamellar compound is produced when the sample has come to equilibrium with the Br_2 or ICl vapor, compounds that are less than saturated can just as well serve as temperature calibration standards.

After having produced a lamellar graphite- Br_2 or graphite- ICl compound, the next step is to remove the compound from the Br_2 or ICl vapor. Once the equilibrium between the sample and the Br_2 or ICl vapor is disturbed, the absorbed intercalate desorbs from the compound. The desorption process continues slowly for about a month in air at room temperature. When the desorption has stopped, the compound is called a residue compound,³ which contains $\frac{1}{3}$ to $\frac{1}{2}$ of the intercalate in the parent lamellar compound. The progress of desorption can be monitored, if desired, by weighing the sample. The desorption time can be considerably shortened by heating the sample¹¹ to $\sim 100^\circ C$ or less as it desorbs in air. Heating to temperatures above $\sim 100^\circ C$ is not recommended, because the sample tends to exfoliate at temperatures above $\sim 177^\circ C$.¹² Because of the stability of residue graphite-halogen compounds in air and in vacuum, this form of graphite-halogens is recommended for use as temperature calibration standards in the electron microscope.

After the bulk residue compound has been prepared, the next step is to obtain a sufficiently thin specimen from the bulk sample for transmission electron microscopy. This process is particularly simple for graphite-halogens, which are layer materials and thus cleave easily along the (001) plane. A sufficiently thin specimen can be obtained by picking up with forceps a small flake that clings to the surface after the surface has been mechanically disturbed by peeling off the surface layers by means of Scotch tape. The flake can directly be placed on the grid of the sample holder of the transmission electron microscope. A flake obtained by using this method typically has a part of its area near the edge sufficiently thin for transmission electron microscopy.

Because the residue compound is stable in air, a bulk residue compound can be used many times; a flake can be obtained from the bulk material whenever a temperature calibration standard is needed.

III. PROCEDURE OF TEMPERATURE CALIBRATION

Graphite- Br_2 and graphite- ICl are to be used for calibration at $100 \pm 1^\circ C$ and $41 \pm 1^\circ C$, respectively. Since both temperatures are above room temperature, a heating sample holder of the transmission electron microscope should be used.

After the electron beam has been focused on a sufficiently thin area of the specimen and a superlattice electron diffraction pattern (Fig. 1) has been obtained, the specimen temperature is to be gradually raised above room temperature. The temperature at which the super-



Graphite



Graphite- Br_2



Graphite- ICl

FIG. 1. Room temperature electron diffraction patterns of pristine graphite, graphite- Br_2 , and graphite- ICl .

lattice diffraction spots disappear is $100 \pm 1^\circ C$ for the case of graphite- Br_2 and $41 \pm 1^\circ C$ for the case of graphite- ICl . Since the phase transformation is reversible, the above procedure can be repeated on the same specimen.

IV. DISCUSSION

The advantages in the use of graphite-halogens as medium temperature calibration standards for transmission electron microscopy are: (i) specimen preparation is simple (specimen thinning is not necessary); (ii) the superlattice diffraction spots are numerous and the ob-

servation of the disappearance of only one of them is sufficient for temperature calibration.

Although the preparation of bulk graphite-halogen residue compounds takes time, very little work is involved. Furthermore, once the bulk compound is prepared, it can be used practically forever as the source of thin flakes, which serve as standard specimens for temperature calibration.

The main source of error in the temperature calibration technique presented here is the difference in temperature between the specimen and the calibration standard. This difference is a consequence of the differences in thermal properties between the two materials, so that the effect of electron beam heating can be of different degrees to the specimen and the standard. Unless the specimen has thermal properties similar to those

of the standard, error due to this problem should be considered in the temperature calibration.

- a) This work was supported by the Air Force Office of Scientific Research.
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