MAR 12 1963

BNL 6728

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MASTER

ADAPTATION OF A COMMERICAL COUNTER X-RAY
DIFFRACTOMETER FOR INVESTIGATIONS
TO 3000°C*

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INTRODUCTION

The rapid advances in many technologically important areas have not only served to accentuate the increased demands for high temperature metals and ceramics but have necessitated a more thorough knowledge of their physical properties when exposed to high temperature service. Toward this latter end, the use of X-ray diffraction has proved an invaluable tool in providing data of regions of thermal stability, expansion coefficients, solid solubility limits, and phase transformations by direct examination at temperature. Since this Laboratory has for some time now been engaged in the study of refractory nuclear materials, it was thought desirable to employ and possibly extend this technique to temperatures ranging up to 3000°C. This communication will describe the equipment developed for this purpose, with experimental results to be described in subsequent publications.

The materials we were chiefly interested in all contain heavy elements and therefore would lead to high X-ray absorption errors if the usual film techniques were used. Furthermore, it was important to reach as high operating temperatures as possible. This made it desirable to collect the necessary data as rapidly as is consistent with good practice. For this reason, it was felt that counter diffractometer rather than film techniques should be used.

For reasons of economy and convenience, it was decided to adapt as much as possible commercially existing equipment. As a basis, a General Electric XRD-5 diffractometer, equipped with a scintillation counter and pulse height discriminator, was used. To this was attached a highly modified version of the Model X-86G high temperature diffractometer attachment manufactured by the Materials Research Corporation. The remainder of this report will be concerned with the modifications which were necessary in order that X-ray diffraction analysis could be carried out at temperatures ranging to 3000°C.

DESCRIPTION

As supplied by the manufacturer, the unit is essentially a water-cooled cylindrical chamber fitted with a pair of 0.030-inch thick demountable beryllium windows. Housed within the chamber is a set of water-cooled, chrome-plated copper jaws which serve as electrical terminals for the specimen stage; the stage itself is constructed of a metal ribbon filament. The jaws are attached through an insulating machinable ceramic-supramica 500 to an alignment device which permits filament translation normal to the specimen surface as well as limited rotation around the direct X-ray beam direction. Provision is made for operation of the chamber under vacuum and for the determination of that vacuum.

It was found that the beryllium window-aluminum frame assemblies on the original equipment tended to leak under vacuum, particularly after prolonged use and repeated tightening of the frames. By substituting stainless steel frames and 0.010-inch thick beryllium sheet, cemented in place with an epoxy resin, vacuums of 10^{-6} Torr could easily and repeatedly be maintained at room temperature. The reduction in thickness of the beryllium windows offered the additional advantage of increasing X-ray transmission by some 15%.

In the original equipment, a hole in the diffractometer furnace cover fitted with a glass window permitted visual and pyrometric observations of the heated specimens. Due to the close proximity of this window to the heated filament it soon became coated during operation due to metal vapor deposition. To eliminate these difficulties a new viewing port, which is shown in Figure 1, was designed. It was made of pyrex, the assembly consists of an inner and outer chamber, both open to the vacuum of the furnace. The outer chamber is double walled, thus effectively forming a dewar flask when evacuated. It is normally filled with liquid nitrogen during operation. The inner chamber which forms the sighting tube, is coated with lampblack to rid the system of internal reflections. Since it is surrounded with liquid nitrogen it helps improve the vacuum and prevents vapor deposition on the optical window. The large bulge at the top was incorporated to diminish liquid nitrogen evaporation losses. In use the trap would crack occasionally in the narrow section where it was joined to the sighting tube. This is due to water collecting and freezing upon addition of liquid nitrogen. This was prevented by blowing a slight bulge at this point as diagrammatically shown in Figure 1.

The sighting tube assembly mounted on the furnace cover with a neoprene o-ring is shown in Figure 2a. Also indicated, at the top of the tube, is a pyrometer filter and/or right angle prism

combination which is placed over another o-ring seal. This arrangement allows 360° prism rotation under vacuum thus facilitating visual and pyrometric observations.

Cooling water and electrical power for the jaw assembly were originally brought in via copper tubing which was suitably insulated from the chamber body. The asymmetrical positioning of the tubing, coupled with its work hardening upon a few translational adjustments, resulted in a "swinging-gate" type of movement rather than the intended pure translation parallel to itself. This was almost entirely remedied by connecting the jaws to the tubing through a short length of flexible copper bellows (see Figure 2b).

The symmetrical flat ribbon filament, used as the heating element in the diffractometer attachment as supplied, is formed with two U-shaped bends and a tab at either end. The edges of the flat central portion of the ribbon upon which the powder specimen is placed are folded down (or up) to provide additional rigidity. According to Intrater and Hurivitt⁽¹⁾, these bends in the filament compensate for thermal expansion so that there is negligible displacement of the specimen from the diffractometer focusing circle upon heating. Further discussion of this important assumption will be considered in some detail later in this paper.

Although pure Pt or one of its Rd alloys provides an excellent material for use in vacuum and oxidizing atmospheres at temperatures up to 1600°C , other filament materials had to be found for higher temperature service. Ta, Mo and W exhibit serious oxidation resistance problems. The latter two were immediately rejected because they presented, in addition, serious fabricating difficulties. Although the Ta filaments had been used successfully, rhenium proved to be more tractable. Its malleability, high melting point (3167°C) and lack of reactivity at high temperatures with the materials in we are interested, made its use seem promising. Although its

oxidation resistance is superior to the aforementioned metals, its use is restricted to neutral or reducing atmospheres.

To facilitate and speed specimen preparation and filament annealing, an auxilliary vacuum system was constructed separate from the diffractometer. This contained a water-cooled copper jaw assembly identical to that found in the camera under a bell jar. The bell jar arrangement also provided both vertical and horizontal observations of the filament.

Initial experiments in this system with the Pt and Ta filaments supplied by the manufacturer revealed considerable temperature variations across the length of the filament. This was not entirely unexpected in view of the short filament length necessitated by the camera design and the conduction losses through the water-cooled jaws. At low temperatures ($\sim 750^{\circ}\text{C}$) a large gradient from the hot central portion of the stage was noted. As the temperature is raised and radiative losses become appreciable the gradient actually decreases because of the containment of radiation within the folds thus counterbalancing the conduction losses at the ends. At still higher temperatures the containment overrides the conduction and the filaments were found to consistently burn out at the folds. The cross-over point of uniform temperature could be systematically changed by varying the "degree of openness" of the folds. Although it is feasible to use a number of filaments with varying fold characteristics to obtain reasonable temperature uniformity and also cover a 3000°C temperature range, this practice would be time-consuming and cumbersome. By tapering the filament ends and using open folds the low temperature conduction losses and the high temperature radiation containment were minimized. Optical pyrometer scanning of a number of filament surfaces indicated a maximum gradient of 5° at 800°C and 10° at 2300°C . These modifications thus provided a single uniformly heated filament operable over a wide temperature range.

The major problem which confronts most high temperature research still remained, however, that of determining the temperature with sufficient precision. Up to temperatures of 1600°C noble metal thermocouples have found widespread use. More recently, the development of W-W26%Re has appreciably extended the range to nearly 2800°C . For our application, however, the normal defects of thermocouples, such as changes in composition, contamination and heat losses through the leads, become further accentuated since the thermo-element must be in direct physical contact with the heated surface of the thin, high-thermal conductivity metal. The use of an optical pyrometer at temperatures above 800°C seemed more promising since it does not contact the specimen. However, the specimen is not in a black body environment when mounted in the X-ray diffractometer. In addition, neither the emissivity of the specimen nor its variation with temperature is normally known with adequate precision. This presented a difficult problem which was solved by further modification of the filament.

Two identical ribbon filaments with their ends trimmed to a 10° taper were die cut from 0.003 to 0.005-inch thick rhenium. They were then die-formed so as to have a shallow rectangular tray in the center with a small, 0.014-inch diameter semicircular channel leading from it (Figure 3). One section was then inverted over the other and the two were spot-welded together. This formed a small chamber with an 0.014-inch internal diameter tunnel leading from it. The tunnel opening effectively acted as a black body. This was qualitatively confirmed by the inability to focus a micro-optical pyrometer within the heated chamber. The emissivity calculated according to the treatment of Gouffe and DeVos⁽²⁾ was 0.99_9 , further confirming black body conditions. Other calculations based on the thermal and electrical properties of metallic rhenium metal and the physical geometry of the filament indicated the outer filament surface to be within a fraction of a degree of the indicated

black body chamber temperature. To check this, melting points of spectrographic grade copper and silver powders on a Re filament were determined pyrometrically and observed to be within 2°C of their accepted values of 1083 and 960.5°C . Also, as will be shown in a subsequent publication, the thermal expansion data obtained for platinum to 1730°C are in excellent agreement with the best recently established values.

Use of this latter fact to confirm the validity of the black body hypothesis assumes any errors associated with the interplanar spacings are either insignificant or fortuitously compensate for the errors in temperature measurement over a wide range.

A major source of error in the measurement of such interplanar spacings is the expansion of the specimen surface away from the diffractometer focusing circle. This was checked with a cathetometer equipped with filar optics and capable of measuring displacements of 2 microns. The expansion normal to the specimen stage which was observed amounted to a maximum correction of less than 0.02° in 2θ at 1650°C for well resolved high-angle peaks ($2\theta > 100^{\circ}$) used in the determination. It is thus felt that above 750°C the use of the radiation emanating from the chamber provides a reliable indication of the true (black body) filament temperatures.

Temperature measurements below 800°C are made with 1/2 mil Pt-Pt 10% Rd thermocouple spot-welded to the stage. The small diameter wires decreased considerably the thermal conduction losses due to the leads. Calibration of thermocouple temperature vs. black body chamber temperature indicated that an error of $\sim 10^{\circ}\text{C}$ at 800°C , which increased to $\sim 25^{\circ}\text{C}$ at 1300°C , still existed. A least squares polynomial fit of the error as a function of temperature gave an empirical correction for use below 800°C . Periodic checks at 800°C provide a convenient means of detecting any alterations in the thermocouple's emf characteristics.

In practice, the filaments were easy to fabricate once the required dies were made. The manufacture of the dies was a simple, machine shop operation because high precision is not required.

Temperature regulation is achieved by supplying power to a step-down transformer through a voltage regulator while maintaining the water-cooling constant by means of a pressure regulator. With a constant thermal load provided by an annealed filament and a constant input voltage, temperature fluctuations were negligible. This was particularly true over short time periods such as those necessary to scan only one reflection slowly. A current of 150A at 10 volts was necessary for the rhenium filament to reach 3000°C.

Using the basic Material Research Corporation's unit with the modifications described above, we have obtained diffraction data for cubic ThO_2 and hexagonal rhenium metal at temperatures up to 3000°C. The data obtained will be published subsequently.

ACKNOWLEDGEMENTS

The authors are indebted to Drs. J. Powell and M. Steinberg for their interests and valuable discussions. Also, we wish to thank Mr. D. Noonan for his experimental assistance.

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FIGURES

- Figure 1 Construction of the sighting tube and cooling chamber
- Figure 2 High temperature diffraction apparatus
- Figure 2a Outside view showing cooling chamber and sighting
 tube capped with prism
- Figure 2b View of diffraction chamber showing filament mounted
 in position and copper bellows on power and water
 cooling leads
- Figure 2c Top view of mounted filament
- Figure 3 Construction of the filament

DIMENSIONS EXPRESSED IN CENTIMETERS

Fig 1

a

b

c

Fig 2

PLATINUM ENDS

FILAMENT ASSEMBLY
4x SCALE

STEP ONE
BLANK 2 REQ'D.

STEP TWO
DIE FORMED BLANK
2 REQ'D

STEP THREE
2 DIE FORMED BLANKS
SPOT WELDED BACK TO BACK

STEP FOUR
DIE PUNCHED TO 10° TAPER

FILAMENT FABRICATION
4x SCALE

Fig 3