Neither of these deductions appears physically necessary; in fact there is evidence that neither is true. J. C. Bokros (private communication) has measured $I(\phi)$ for several pyrolytic graphites and has obtained some intersecting curves. Fig. 3 is an SEM photograph of the basal-plane surface of a piece of Union Carbide highly oriented pyrolytic graphite (HOPG) which has been slightly oxidized. A hole burned in the surface of the region shown reveals a crystallite almost exactly perpendicular to the deposition plane.

It should be noted that the magnetic-susceptibility data do not prove the validity of the BAF measurements since the magnetic-susceptibility tensor is obviously changing with heat-treatment temperature (Table 4), and obviously no independent measure of $\chi_2$ and $\chi_c$ is possible. However, the data presented lend strong support to the measured anisotropy.

All samples investigated here have quite a high degree of preferred orientation. The data of Tassone, fitted by Ergun & Schehl to $I_2(\phi) = (1 - b^2 \sin^2 \phi)^{-1}$, are for relatively isotropic pyrolytic carbons used to coat nuclear-fuel particles. It is therefore possible that the orientation function of poorly oriented pyrolytic graphites is best represented by $I_2(\phi)$, as originally suggested by Ruland (1967), whereas that for well oriented samples is best represented by $I_1(\phi)$.

The results presented here show that for a quick BAF determination the orientation function $I(\phi)$ for highly oriented pyrolytic graphites may be approximated by $\cos^m \phi$, with $m$ determined from $\phi_{12}$. For really accurate BAF measurements there is no substitute for a complete determination of $I(\phi)$ followed by numerical integration. However, the accuracy required to measure $I(\phi)$ at large $\phi$ may be beyond the sensitivity of the apparatus or may not warrant the time involved.

We wish to thank Mr G. Rellick for carrying out the controlled oxidations of the cylindrical specimens. W.S.H. wishes to express his appreciation to the Department of Material Sciences, The Pennsylvania State University, for the opportunity to be a guest worker for a period of time.

References


The Analysis of Hydrides in Hydrogen–Zirconium Alloys Cooled from the α-Zirconium Phase Field

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An X-ray powder diffraction method is described which can determine the phases present in hydrogen–zirconium alloys containing ≥ 100 p.p.m. hydrogen. The method is applied to show that γ- and δ-phase hydrides are formed when hydrogen–zirconium alloys are cooled from the α-phase field. It is shown that quenching favours the formation of the γ phase.

Introduction

The occurrence of γ zirconium hydride (f.c.t.) at the high-hydrogen end of the hydrogen–zirconium system has been studied by several workers using X-ray diffraction (Beck, 1962; Moore, 1969; Barraclough & Beevers, 1970). The only X-ray investigations of the occurrence of this phase at the low-hydrogen (i.e. ≤ 1000 p.p.m.)
end of the system are due to Bailey (1963) who prepared samples by cooling at various rates from the β-zirconium (b.c.c.) phase field and Sidhu, Heaton, Campos & Zauberis (1962) who have briefly reported work on the zirconium–deuterium system down to 400 p.p.m. deuterium.

In this work an X-ray powder diffraction method is described which is applicable to the phase analysis of hydrogen–zirconium alloys which contain as little as 100 p.p.m. hydrogen (1 at. % hydrogen). Samples prepared in the α-zirconium phase field and cooled to room temperature at various rates have been examined by this method and the phases present established on a semi-quantitative basis.

**Experimental**

Samples were prepared by successively cold rolling and annealing in a vacuum 1.6 mm thick UKAEA reactor-grade zirconium (ex-sponge) sheet until it was 400 μm thick. A typical analysis of this material is given in Table 1.

X-ray diffraction failed to detect any phase other than α-zirconium (h.c.p.) in this material and it was concluded that the oxygen (± 1 at. %) was in solid solution.

The zirconium sheet was hydrided by the addition of predetermined amounts of hydrogen (purified by passage through a silver-palladium diffusion leak) at 550°C in a Sievert's apparatus similar to that described in Mueller, Blackledge & Libowitz (1968). The samples were held at 550°C for 2 to 4h to ensure equilibration at this temperature which corresponds to the maximum solubility of hydrogen in α-zirconium. The samples were cooled at various rates. Slow cooling merely represented cooling overnight, fast cooling involved running the furnace away from the furnace tube. Quenched samples were encapsulated in Pyrex at 10⁻⁵ torr, reheated for 18 to 24 h, removed rapidly from the furnace, and crushed in iced water.

The X-ray specimens were made by reducing specimens 2 × 1.5 cm × 500μm in size to a thickness of about 50μm by mean of a solution of 45 parts of distilled water, 45 parts AnalR 70 % w/w nitric acid, and 10 parts of 40% redistilled aqueous hydrofluoric acid. This thickness is a compromise which allows adequate X-ray penetration of the specimen in the Nonius camera while retaining a sample representative of the bulk material.

The X-ray diffraction study was not straightforward and it is worth emphasizing the difficulties which were encountered and how they were overcome. The Debye–Scherrer method was not used as it lacked sufficient resolution and sensitivity; moreover the X-ray source must be excited at less than 18 kV to avoid fluorescence of the zirconium in the bremsstrahlung. X-ray diffrac-

![Fig. 1. The effect of hydrogen content and cooling rate on the amount of γ-phase in hydrogen-zirconium alloys.](image)

**Table 1. Analysis of zirconium sheet starting material in p.p.m.**

<table>
<thead>
<tr>
<th></th>
<th>O₂</th>
<th>N₂</th>
<th>H₂</th>
<th>Hf</th>
<th>Sn</th>
<th>Fe</th>
<th>Ni</th>
<th>Cr</th>
<th>Al</th>
<th>Ti</th>
<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1300</td>
<td>80</td>
<td>20</td>
<td>400</td>
<td>&lt; 50</td>
<td>380</td>
<td>40</td>
<td>&lt; 100</td>
<td>100</td>
<td>&lt; 30</td>
<td>&lt; 20</td>
</tr>
</tbody>
</table>
tometry was unsuitable because of strong preferred orientation in the foils which led to the appearance of a series of confusing minor signals caused by contamination of the X-ray source (with Fe, W, etc.). Furthermore, in addition to a very strong 002 reflexion the forbidden 001 α-zirconium reflexion was visible. Perhaps this was due to a mis-stacking phenomenon in the zirconium although space-group forbidden reflexions have been observed from such simple structures as diamond (Taylor, 1971) and silicon.

A Nonius–Guinier–de Wolff Quadruple-focusing camera, Mark II, was successfully used. Now the quartz monochromating crystal reflects not only Cu Kα radiation (wavelength 1.54 Å) but also any harmonics of it present in the bremsstrahlung. Generally the second harmonic (α/2) (wavelength 0.77 Å) is so feeble that it can be disregarded. However, when a Cu Kα beam passes through a 50μm zirconium foil its intensity, Iα, is attenuated by 99% while α/2 is attenuated by only 21%. Thus whereas Iα: Iα/2 in the incident beam was about 1:0.005 it became 1:0.43 after diffraction and transmission by the foil. Consequently the search for hydrides is hindered not only by interference from the Cu Kα diffraction pattern of α-zirconium but also by the corresponding α/2 diffraction pattern. The second harmonic can, however, be eliminated by running the X-ray source at rather less than twice the excitation potential of Cu Kα. Consequently the X-ray photographs were obtained with double-coated Ilford Industrial X-ray film exposed for 228 h using a fine-focus copper X-ray tube run at 12 kV and 26 mA on a Philips PW 1010 X-ray generator.

Measurements were made with a d-rule and a modified Kodak Coldlight Illuminator fitted with a 55 W SOX Atlas sodium light. This illuminator is particularly useful when very faint X-ray reflexions are being sought and measured. It is believed that its superiority results from the way in which monochromatic light, as opposed to white light, is diffracted by the grains in a photographic emulsion.

Phase analyses were carried out by comparison with published data (Mueller, Blackledge & Libowitz, 1968): in the case of the γ-hydride the 111, 200 and 202 reflexions were identified while the 111, 200, 220 and 311 reflexions were found corresponding to δ-hydride. The chemical composition of the 250 p.p.m. hydrogen samples was linked with the visually estimated intensities of the 111, γ- and δ-phase reflexions to give semi-quantitative phase analyses on all the specimens examined. These reflexions were selected for comparative examination because they were adjacent and their calculated X-ray intensities differed by only 4%.

Results

The results, given in Table 2 and Figs. 1 and 2, show that both γ- and δ-hydrides are formed when hydrogen–zirconium alloys, which contain as little as 100 p.p.m. of hydrogen, are cooled from the α-phase field to room temperature. The quantity of γ-hydride in the quenched

![Graph](image-url)

Fig. 2. The effect of hydrogen content and cooling rate on the amount of δ-phase in hydrogen–zirconium alloys.
samples increases as the hydrogen content increases (Fig. 1). Consequently, quenching inhibits the formation of the δ-hydride. Similar results were reported briefly by Bailey (1969) and by Bradbrook, Lorimer & Ridley (1972) on the basis of electron diffraction.

Table 2. The variation of the amounts of γ- and δ-hydrides as a function of composition and cooling rate

<table>
<thead>
<tr>
<th>Hydrogen content*</th>
<th>Cooling rate</th>
<th>Estimated p.p.m. hydrogen combined as</th>
<th>γ-phase</th>
<th>δ-phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>p.p.m.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>slow</td>
<td>60</td>
<td>250</td>
<td></td>
</tr>
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<td>100</td>
<td>fast</td>
<td>trace</td>
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<td>quench</td>
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<td></td>
</tr>
<tr>
<td>600</td>
<td>quench</td>
<td>600</td>
<td>40</td>
<td></td>
</tr>
</tbody>
</table>

* These figures represent the amount of hydrogen added. Their validity has been cross-checked by analyses on other samples.

Discussion

Beck (1962) concluded that γ-hydride is formed as an intermediate phase in the decomposition of δ-hydride to α-zirconium. This view is supported by Barraclough & Beevers (1970) and by Moore (1969) who showed that under certain conditions the γ-hydride to δ-hydride reaction is reversible. The results reported here show additionally that the γ-phase can be formed via the decomposition of the α-phase.

Motz (1962) has suggested that the γ-hydride is merely an undercooled α-hydride (b.c.t.). This seems unreasonable since the α-hydride contains at least 59 at. % hydrogen which is incompatible with the composition of the preparations described here.

Since the three phases: hydrogen-saturated α-zirconium, γ- and δ-hydrides cannot be in thermodynamic equilibrium in a two-component system, except at an invariant point, it is reasonable to suggest that their co-existence may be based on a combination of phase equilibrium and kinetic considerations. Thus if the δ-hydride is stable above ≈ 294 °C as indicated by Moore (1969), while the α → δ and δ → γ reactions are sluggish but the α → γ is fast, it is evident that quenching will favour the formation of the γ-hydride which will be retained at room temperatures. The slower cooling rates are relatively much less successful in doing this, as the samples then spend too long in the α + δ-phase region and the δ-hydride formed fails to complete the transition to the γ-hydride on further cooling.

Conclusions

The fact that the γ-hydride can be prepared at both low (1 at. %) and high (62 at. %) hydrogen concentrations in the hydrogen–zirconium system suggests that a careful study should be made of the γ → δ transition over a wide range of temperatures and compositions in an attempt to establish the existence of a γ-hydride field in the phase diagram rather than to regard the γ-hydride merely as a metastable intermediate in the decomposition of one of the hydrogen-containing phases α, δ or ε.

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References