SINTERED MATERIALS AND COMPONENTS

THE PREPARATION OF LOW-POROSITY SPECIMENS OF TITANIUM AND ZIRCONIUM HYDRIDES BY THE METHOD OF REACTIVE SINTERING

M. M. Antonova

Institute of Materials Problems, Academy of Sciences, UkrSSR
Translated from Poroshkovaya Metallurgiya, No. 7 (31), pp. 25-33, July, 1965
Original article submitted July 8, 1964

In order to study the properties of hydrides and their practical applications, it is necessary to prepare dense hydride specimens. In the literature, only two works have been reported on the preparation of dense zirconium hydride specimens [1, 2], and no information is available on the preparation of other dense hydrides. Because of their thermal instability, hydrides cannot be produced by the standard powder metallurgy methods (sintering, hot pressing). However, there are several methods of producing hydrides of the transition metals in the dense form, which include very slow hydrogenation of dense metallic specimens, sintering of hydride compacts in a hydrogen atmosphere, followed by further hydrogenation at low temperature, and reactive sintering analogous to sintering for the preparation of nitride specimens [3]. All three methods of preparation of dense zirconium hydride specimens were studied in [1], and the method of reactive sintering was found the most promising. The above-mentioned paper does not contain a detailed description of the reactive sintering of zirconium hydride with an examination of all factors influencing the sintering process. It thus became necessary to carry out an additional, fuller study of this process.

In the present investigation, a study was made of the possibility of obtaining dense specimens of titanium and zirconium hydrides by the method of reactive sintering. This method postulates the carrying out of experiments at relatively low temperatures. During the reaction of a metal with hydrogen, a large amount of heat is evolved, as a result of which the specimen temperature is raised by 200-300°C. Because of this, the material becomes more ductile, and is subject to shrinkage due to sintering. The shrinkage compensates the expansion of the metal lattice during hydrogenation, thereby decreasing internal stresses in the specimen and preventing the latter from cracking.

Preparation of Dense Specimens of Titanium Hydride

Titanium hydride begins to dissociate into the metal and hydrogen at a temperature of 500-550°C [5], and is practically completely decomposed at 1000-1100°C. In order to suppress the dissociation of the hydride at these temperatures, it would be necessary to raise the hydrogen pressure to several hundred kilonewtons per square meter. With the above-mentioned method, it is possible to perform sintering at low temperatures and a hydrogen pressure not exceeding 100 kN/m². The isobar of hydrogen adsorption by metallic titanium is shown in Fig. 1, from which it follows that the temperature zone in which a fairly high hydrogen content is maintained lies between 500 and 700°C. * At higher temperatures, the hydrogen content of the hydride sharply decreases, which in turn reduces the exothermic effect of the reaction, thereby indicating that high temperatures are not suitable for the reactive sintering process.

Sintering was performed in a quartz reactor placed in a tubular electric furnace. The reactor was connected with a vacuum system on the one hand and a hydrogen feed system on the other. The vacuum in the system was measured with a thermocouple potentiometer. The total volume of the system did not exceed 200 cm³. The temperature was measured with a Pt/Pt-Rh thermocouple and was regulated with an EPD-52 potentiometer. Hydrogen was obtained by decomposing titanium hydride.

The study was made on a metallic titanium powder obtained by the reduction of titanium dioxide with calcium hydride; it was 99.99% pure, and had a mean particle size of 150 µ. Compacts of 8-mm diameter and 10-12 mm height were pressed from this powder without a binder. The following relationship between the density and porosity of titanium compacts and compacting pressure was established:

*As in original, although in apparent discrepancy with graph—Publisher.
To regulate the reactive sintering process, the titanium compacts were presintered in a vacuum at 900°C. A substantial shrinkage of specimens was observed at long sintering times (2-4 h). On sintering for 0.5-1 h, i.e., for a length of time normally employed in reactive sintering, the shrinkage of compacts was insignificant, and attained 1.0-1.5% for specimens with an initial density of 2.55-2.60 g/cm³. The low value of shrinkage compared with the growth of volume during hydrogenation (about 15%↑) indicates that the process of reactive sintering of titanium is governed by the hydrogenation process. In order to discover the optimum conditions of preparation of dense hydride specimens, the author examined the effect of sintering temperature and duration, the initial roasting of starting compacts in a vacuum, the rate of hydrogen feed into the reaction zone, and the subsequent additional hydrogenation of specimens at low temperature on the reactive sintering process. The results of these studies are presented in the tables.

As can be seen from Table 1, with increasing initial porosity, the final porosity of specimens also increases, although their relative shrinkage decreases. Hydrogen content slightly increases with decreasing initial porosity, but remains within the limits of the homogeneity region of the TiH₂ phase [5]. A porosity of less than 25.9% cannot be obtained, because the specimens crack when the density of the starting compacts is further increased. Subsequent experiments were performed with compacts having an initial density between 2.90 and 3.30 g/cm³. The cracking of specimens with an initial density of more than 3.07 g/cm³ was prevented by prior roasting.

Decreasing the sintering time from 60 to 7 min at a rapid feed of hydrogen has no effect on the hydrogen content and density of the final product. Sintering for 7 min is quite adequate for the completion of the process (Table 2).

With increasing temperature, the hydrogen content of the final product decreases, and the specimen density increases (Fig. 2). By changing the temperature, it is possible to obtain specimens with different amounts of hydrogen, but specimens produced at low temperature and containing more than 63 at.% hydrogen are susceptible to cracking, as a result of which it is not advisable to lower the temperature below 600°C (Table 3).

Prior vacuum roasting of compacts helps to drive off the gases adsorbed on the surface and dissolve the surface oxides usually present in powders in the metallic lattice. Because of these processes, the metal surface becomes purified and more active. Roasting was carried out at 900°C for 60 min, until pressure in the system reached 0.133 N/m². Table 4 shows results of the reactive sintering of specimens subjected to prior vacuum roasting. It also contains data obtained in experiments involving the additional hydrogenation of specimens after sintering.

**TABLE 1. Effect of Initial Density of Compacts on Final Density and Hydrogen Content of Specimens (sintering for 60 min at 600°C without prior roasting)**

<table>
<thead>
<tr>
<th>Initial density, g/cm³</th>
<th>Initial porosity, %</th>
<th>Final density, g/cm³</th>
<th>Final porosity, %</th>
<th>Hydrogen content mass %</th>
<th>at.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.22</td>
<td>51.2</td>
<td>1.82</td>
<td>59.0</td>
<td>0.73</td>
<td>26.1</td>
</tr>
<tr>
<td>2.56</td>
<td>43.6</td>
<td>2.22</td>
<td>40.0</td>
<td>3.29</td>
<td>62.0</td>
</tr>
<tr>
<td>2.71</td>
<td>40.3</td>
<td>2.36</td>
<td>38.7</td>
<td>3.39</td>
<td>62.5</td>
</tr>
<tr>
<td>2.82</td>
<td>37.9</td>
<td>2.51</td>
<td>34.5</td>
<td>3.46</td>
<td>63.0</td>
</tr>
<tr>
<td>3.06</td>
<td>29.6</td>
<td>2.79</td>
<td>25.6</td>
<td>3.50</td>
<td>63.5</td>
</tr>
<tr>
<td>3.07</td>
<td>32.4</td>
<td>2.80</td>
<td>25.9</td>
<td>3.64</td>
<td>64.1</td>
</tr>
</tbody>
</table>