March 1, 1960 V. L. STOUT ET AL 2,926,981

METHOD OF GETTERING USING ZIRCONIUM-TITANIUM ALLOY

Filed Sept. 11, 1957

Fig. 1.

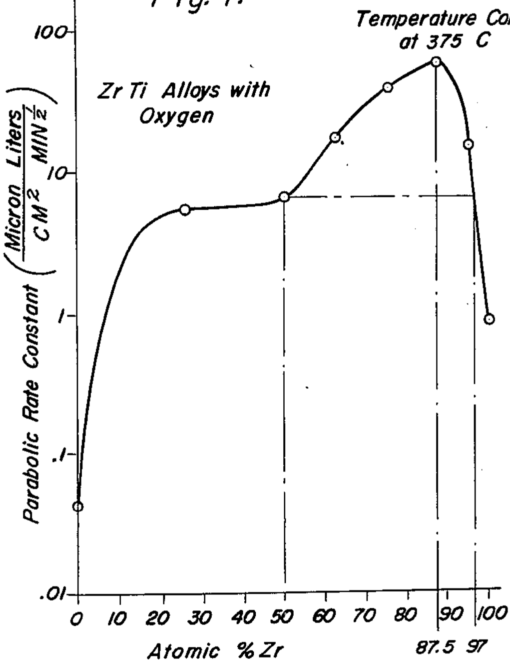


Fig. 3.

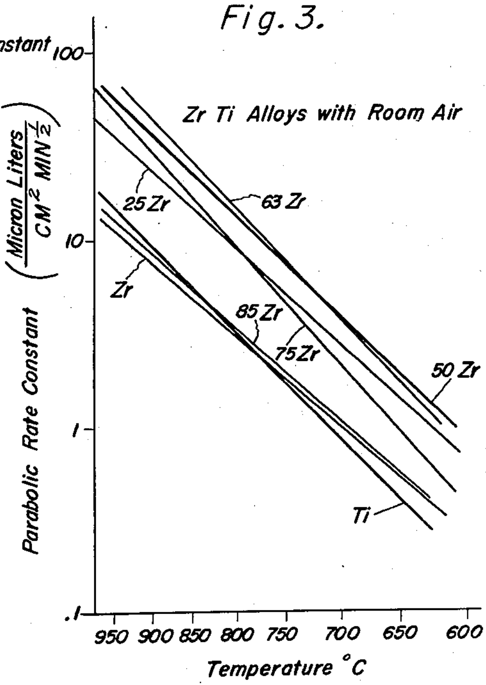
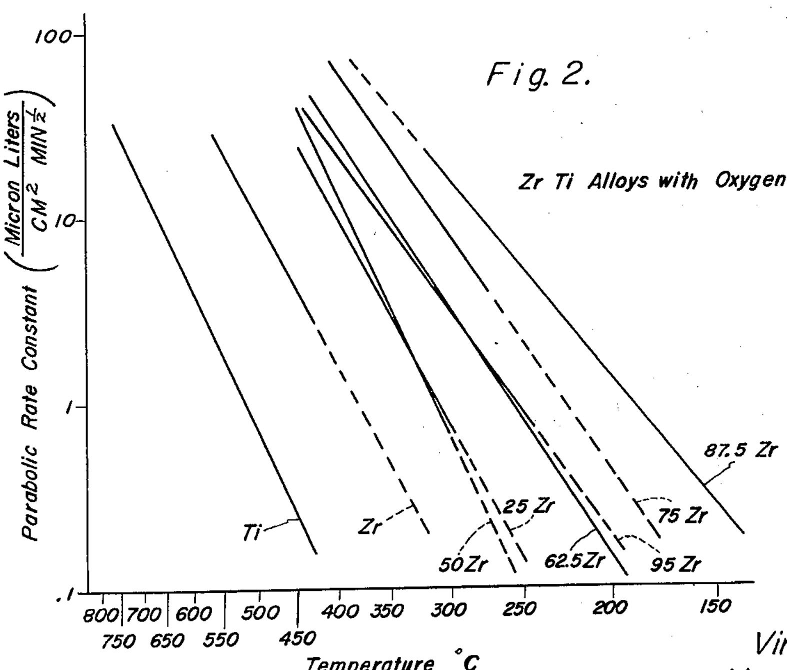


Fig. 2.



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METHOD OF GETTERING USING ZIRCONIUM-TITANIUM ALLOY

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4 Claims. (Cl. 316—25)

The present invention relates to improved getter materials and more particularly to the use of zirconium-titanium alloy getters.

Because tube failures often result from residual gases and vapors, there is a continual effort to discover more efficient getter materials.

Accordingly, an object of the present invention is to provide a more efficient getter material.

Another object is to provide a method of gettering with a more efficient getter material.

Titanium and zirconium are known to rank among the best of getter materials but even they have severe limitations. For example, titanium does not continuously sorb hydrogen, in the gettering of water vapor, unless heated to a temperature so high that the surface oxidation, which inhibits sorption of hydrogen, is continuously sorbed. But at such a temperature, titanium retains only a small amount of hydrogen.

Thus, a further object of the present invention is the provision of a method of gettering with a getter material that sorbs oxygen much better than either titanium or zirconium.

Still another object is the provision of a getter material that sorbs water vapor much better than either titanium or zirconium.

Many getter materials, such as titanium in the sorption of oxygen, are effective at only high temperatures.

Therefore, still another object of the present invention is to provide a getter material that is effective at relatively low temperatures.

The above objects are achieved in one form of our invention by using an alloy of zirconium and titanium. Although any alloy of these materials makes a good getter for oxygen, water vapor, and air, best gettering for these substances is had if the amount of zirconium is within the range of 50 to 97 atomic percent. To be more specific, the optimum alloy is approximately 87.5 atomic percent zirconium for the gettering of water vapor or oxygen, and 50 to 63 atomic percent zirconium—the exact percentage depending upon the temperature—for the gettering of air.

Although the specification concludes with claims particularly pointing out and distinctly claiming the subject matter that we regard as our invention, the invention may be better understood from the following description taken in connection with the accompanying drawing in which:

Fig. 1 is a graph of the oxygen sorption constant of zirconium-titanium alloys at 375 degrees centigrade,

Fig. 2 is a graph of the oxygen sorption constant of several zirconium-titanium alloys over a range of temperatures, and

Fig. 3 is a graph of the air sorption constant of some zirconium-titanium alloys over a range of temperatures.

In the graph of Fig. 1 the ordinate units are micron liters of sorbed oxygen per centimeter squared of getter surface per minute to the one-half power. These units

are obtained from the basic equation for the sorption of gases and vapors, which is:

$$Q=Kt^{1/2} \quad (1)$$

wherein Q is the quantity of gas or vapor sorbed per unit area of getter surface; K is a constant—called the parabolic rate or sorption constant—the value of which depends upon, among other things, the particular gas or vapor and temperature of interest; and t is the time during which sorption occurs.

The derivative of Equation 1 with respect to time is the rate

$$\frac{dQ}{dt}$$

of gas or vapor sorption:

$$\frac{dQ}{dt}=\tfrac{1}{2}Kt^{-1/2} \quad (2)$$

Thus, K is a measure or indication of sorption rate and consequently has been selected for the ordinate values of the Fig. 1 graph.

The abscissa units of Fig. 1 are in atomic percent zirconium. That is, they are the number of atoms of zirconium in the respective alloys, divided by the sum of the number of atoms of titanium and zirconium.

The graph of Fig. 1 illustrates that most zirconium-titanium alloys at 375 degrees centigrade have a higher oxygen sorption constant than either titanium or zirconium alone. In the region from 50 to 97 atomic percent zirconium, the sorption constant is especially high. And at approximately 87.5 atomic percent zirconium, the oxygen sorption constant, which is a maximum, is almost 100 times greater than that for substantially pure zirconium and approximately 1,000 times greater than that for substantially pure titanium.

The lines in Fig. 2 represent the oxygen sorption constants for the indicated zirconium-titanium alloys over a large range of temperatures. The solid-line portions are the loci of plotted points, but the dotted portions are only extrapolations from the solid-line portions. The extreme right position of the 87.5 atomic percent zirconium line signifies that over the indicated range of temperatures a zirconium-titanium alloy of this percentage has a greater oxygen sorption constant than that for any other alloy tested. Also, the position of all of the alloy lines to the right of the zirconium and titanium lines means that all of the tested alloys getter oxygen, for any given sorption constant, at a lower temperature than either titanium or zirconium. This is not to say that all zirconium-titanium alloys getter better than zirconium for, as is evident from the curve of Fig. 1, alloys of 10 or less atomic percent zirconium do not getter oxygen as well as substantially pure zirconium.

One deduction obtainable from the approximately parallel relationship between many of the lines of Fig. 2 is that the oxygen sorption constant curve at any temperature has approximately the shape of Fig. 1 because over the range of illustrated temperatures, an alloy of 87.5 atomic percent zirconium has a higher sorption constant than any other tested alloy; an alloy of 75 atomic percent zirconium has a higher sorption constant than 62.5 atomic percent zirconium; an alloy of 62.5 atomic percent zirconium has a higher sorption constant than 50 atomic percent zirconium; etc.

Although the graphs of Figs. 1 and 2 are directed to the sorption of oxygen, they also apply to water vapor because only the sorption of the oxygen of the water molecules presents a problem. Once surface oxidation due to water vapor is dissolved, hydrogen is readily sorbed.

The graph of Fig. 3 is similar to that of Fig. 2 except that it illustrates the sorption constants of air rather than oxygen. Alloys between 50 and 63 atomic percent zirconium are seen to be very good for sorbing air and the optimum alloy depends upon temperature. As is evident from Fig. 1, this percentage range although not optimum, is also good for the sorbing of oxygen and water vapor. Thus, if both water vapor and air are to be gettered, the atomic percentage of zirconium should be selected between 50, which is near the optimum for sorbing air, and 87.5 which is near the optimum for the sorption of water vapor.

These getter materials can be used in the conventional manner. That is, they can be placed in the envelope to be evacuated, and either directly heated by a heater coil or the like, or indirectly heated by radiation and/or conduction from other heated components in the envelope.

What we claim as new and desire to secure by Letters Patent of the United States is:

1. The method of removing vapors and gases from an enclosure, said method comprising the steps of: placing in said enclosure a getter consisting essentially of an alloy of 10 to 98 atomic percent zirconium and the balance substantially all titanium, and heating said getter.

2. The method of removing vapors and gases from an enclosure, said method comprising the steps of: placing in said enclosure a getter consisting essentially of an

alloy of 50 to 97 atomic percent zirconium and the balance substantially all titanium, and heating said getter.

3. The method of removing vapors and gases from an enclosure, said method comprising the steps of: placing in said enclosure a getter consisting essentially of an alloy of 70 to 95 atomic percent zirconium and the balance substantially all titanium, and heating said getter.

4. The method of removing vapors and gases from an enclosure, said method comprising the steps of: placing in said enclosure a getter consisting essentially of an alloy of 87.5 atomic percent zirconium and the balance substantially all titanium and heating said getter.

References Cited in the file of this patent

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