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(54) **Hydrogen Permeation Resistant Phosphate Coatings**

(57) A method for reducing hydrogen diffusion through metal wherein the metal is coated with a phosphate-radical-containing, phosphate-glass-forming material on at least one

surface thereof. The coating is then heated to at least 350°C to form a phosphate glass. This method is especially applicable to nuclear reactors to minimize tritium diffusion. The coating is preferably formed with a solution of phosphoric acid which may also contain compounds such as MnSO₄, SiO₂ and Na₂Cr₂O₇.

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SPECIFICATION

Hydrogen Permeation Resistant Coatings

The present invention relates to coatings for metal, and in particular, to coatings to reduce diffusion of hydrogen (the term hydrogen is used herein in a broad sense and includes the deuterium and tritium isotopes).

While there are a number of operations in which it is desirable to minimize the diffusion of hydrogen through metal (e.g. to lessen hydrogen embrittlement or to lessen leakage in a hydrogen-oxygen fuel cell), the most serious problem is probably the diffusion of radioactive tritium through the metal walls in the primary fluid containing apparatus of a nuclear reactor. This could be a problem especially in fast breeder reactors and in fusion reactors.

One way of reducing the diffusion of hydrogen would be to use piping which either contains substantial amounts of, or has layers of, metal with a greater resistance to the diffusion of hydrogen. Aluminum, for example, has been found to have a 3 orders of magnitude, lower diffusion rate. Such arrangements, however, present problems with regard to fabrication, hot sodium compatibility, and/or cost.

While organic coatings could be used to reduce diffusion somewhat in certain cases, in many cases (including nuclear reactors) such organic coatings are generally unable to withstand the operating conditions (e.g. temperatures of the metal or the radiation).

Another method of limiting diffusion would be to paint a glaze material on the metal, allow it to dry, and then fire the coated metal in a furnace at about 700—1000°C to eliminate the temporary binder and fuse the glaze. Such a process would be relatively expensive and large objects such as reactor piping would be extremely difficult to fire in a furnace. Further, handling and temperature cycling would tend to crack such coatings and render them ineffective.

It is therefore the principal object of the present invention to provide a coating for a metal surface which safely prevents H₂ diffusion.

With this object in view, the present invention resides in a method of reducing hydrogen diffusion through metal, characterized in that: a coating of phosphate-radical-containing, phosphate-glass-forming material is applied to at least one surface of said metal, and said coating is heated to at least 350°C to convert said coating into a phosphate glass.

It has been discovered that coatings containing the PO₄ phosphate radical can be applied to metal surfaces and converted into a diffusion resisting phosphate glass at moderate temperatures. While these coatings can withstand heating to somewhat higher temperatures, the glass is formed in the 350—600°C range. In the case of reactor piping, the coating can be applied by painting a phosphoric acid solution onto the metal reactor piping, installing the insulation, and using the normal heat from reactor operation to form

the glass. The phosphate glass coating is preferably operated in a range in which it is not melted but is softened so that cracking of the glass from temperature cycling is generally avoided. If the phosphate glass is to be operated at above 600°C, additives are preferably used to raise its melting point.

Description of the Preferred Embodiments

While most gases do not diffuse to any significant extent through metals, the diffusion of hydrogen is quite rapid. The diffusion increases with temperature and decreases with atom size (i.e., tritium diffuses slightly slower than deuterium). As tritium is radioactive, even relatively small leakage rates of tritium are significant. Thus, it was decided to experiment with various coatings on the stainless steel normally used for such reactor piping.

Early experiments were performed using a coating of chrome and manganese (both separately and together) with the object of providing materials which would create a protective oxide coating on the surface at operating temperature (the design operating temperature for the piping for the fast breeder reactor in the particular case being analyzed was about 550°C). Pack coating was considered, however, special furnaces would be required for pack coating of these co-metallic layers of chrome and magnesium.

In an attempt to avoid the use of special furnaces, various methods of applying a combined coating of manganese and chrome were tested. One test using a mixture of Na₂Cr₂O₇ and MnSO₄ with H₃PO₄ proved surprisingly effective. The hydrogen permeation rate at 550°C dropped by factor of almost 20 within 66 hours in the test when the above mixture was used. When the tubing was examined after the test, it was seen that the surface of the metal was coated with a thin, almost transparent, glassy layer. Subsequent tests were run with MnSO₄ and H₃PO₄ (eliminating the chromium) and then finally with H₃PO₄ only. The last coating proved to be the most effective hydrogen barrier of all. Thus, it is clear that the testing with manganese, chromium and phosphoric acid showed good results, not because of the manganese or chromium, but instead because of the phosphoric acid.

It appears that a phosphate glass is being formed by reaction of the phosphate radical with metal oxides or metals from the surface which is being coated. This provides a self cleaning action and probably accounts for the extremely good adhesion of the phosphate glass to the metal surface.

It was also found that the surface of the glass softened slightly at operating temperature. It is felt that the thin layer and the softening of the glass both aid in avoiding cracks in the phosphate glass during temperature cycling. The tests also showed that the phosphoric acid (without chrome or magnesium) not only achieved a lower diffusion rate, but also reached this low rate

almost immediately upon being heated. As compared to untreated tubing, the phosphoric acid treatment reduced diffusion by a factor of 50 to 100.

5 In these tests, one-eighth inch stainless steel tubing was coiled into a helix to provide a convenient test volume of a relatively small size. The outside of the tubing was painted with the test solution. The inside of the tubing was first
10 evacuated and then backfilled with hydrogen. The coated assembly was placed in an oven at 550°C. The hydrogen pressure was monitored to determine the diffusion rate.

Untreated stainless steel had a diffusion rate of
15 about 1×10^{-6} cc/sec/cm² of surface/mm of thickness at 550°C with a 10 Torr difference in partial pressure of hydrogen. The diffusion rate for stainless steel coated in the manner of this invention (in the same units) was reduced to
20 1×10^{-8} .

Various concentrations of phosphoric acid from concentrated (e.g. 75% solution) phosphoric acid down to approximately a 20% solution all appeared to be similarly effective. While a single
25 coat of solutions below 5% will reduce diffusion, H₃PO₄ solutions above about 5% for other solutions having at least that phosphate radical concentration are strongly recommended). A small amount of water soluble wetting agent can be
30 added, especially with the more dilute solutions. Other coatings in which the phosphate radical is available at these temperatures can also be used. Thus, ammonium phosphate for example can be used, but calcium phosphate cannot, as the
35 phosphate radical in calcium phosphate would not be available at these temperatures. Portions of the solution which volatilize at these temperatures (such as ammonia, water, or CO₂) will, of course, generally not affect the glass
40 composition.

As noted previously, it is desirable that the phosphate glass soften but not melt at the normal operating temperature of the metal. The melting point of the phosphate glass coating can be
45 adjusted by adding one or more metal oxide compounds to the phosphate radical containing solution, MnSO₄, SiO₂ and Na₂Cr₂O₇ are examples of metal oxide compounds which can be added.

The thickness of the final phosphate glass layer
50 can be adjusted both by adjusting the concentration of the phosphoric acid and the thickness of the coating of the phosphate radical containing material applied to the surface. The thickness of the coating can be adjusted by
55 changing the viscosity by, for example, adding small amounts (e.g., 1%) of a volatilizable thickener such as hydroxyethylcellulose. Generally, however, this is unnecessary as even extremely thin layers of phosphate glass give
60 sufficient reductions in hydrogen diffusion rate.

The invention is not to be construed as limited to the particular forms described herein, since these are regarded to be illustrative rather than restrictive.

65 Claims

1. A method of reducing hydrogen diffusion through metal, characterized in that a coating of phosphate-radical-containing, phosphate-glass-forming material is applied to at least one surface
70 of said metal, and said coating is heated to at least 350°C to convert said coating into a phosphate glass.

2. A method as claimed in claim 1, characterized in that said coating consists essentially of an H₃PO₄ solution.

3. A method as claimed in claim 1, characterized in that said coating consists essentially of at least one metal oxide compound in an H₃PO₄ solution.

4. A method as claimed in claim 1, wherein
80 said metal is at least part of a nuclear reactor primary fluid containing apparatus and the hydrogen whose diffusion is to be reduced is in the form of tritium and wherein said metal is stainless steel, characterized in that a single coat
85 consisting essentially of 20—75% H₃PO₄ solution is used as the coating.

5. A method as claimed in claim 4, characterized in that said heating to at least
90 350°C is provided by operating the reactor wherein said metal is heated to a temperature between 350°C and 600°C such that said phosphate glass is maintained above its softening point but below its melting point.