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TREATMENT OF STEAM FOR THE PROTECTION
OF CERTAIN METAL PARTS

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This invention relates to the treatment of steam generally, for example, in steam power plants for the generation of electric power, and more particularly to the provision of a gas atmosphere within the system, having limited oxidizing potential to prevent the formation of the volatile trioxides of certain metals such as molybdenum and tungsten and their alloys.

The trend in modern power generation equipment is towards higher operating temperatures and pressures. In particular, in steam generating equipment, pressures and temperatures have now reached about 1800 p.s.i. and 1100° F. In a steam power system employed for the production of electrical power and using turbines to convert the energy of the steam into electrical power, serious problems are encountered in the choice of metals that are able to withstand high temperatures in a steam atmosphere without weakening or deteriorating after extended periods of operation. Included among the more desirable metals which will maintain their strength at high temperatures are molybdenum and tungsten and their alloys. However, the particular disadvantage of these metals is that upon exposure to steam at high temperatures, a trioxide forms on their surfaces which is extremely volatile above a temperature of about 1000° F. and, consequently, continual corrosion of these parts takes place. One means of utilizing the high strength characteristics of these metals is by enclosing these metals within a protective coating which has a satisfactory resistance to corrosion. Such coatings need not have a high resistance to sustained loads of long duration since the underlying base metal will provide this. The disadvantages of protective coatings are that they may be fragile and unable to withstand mechanical impact or abrasion, or they may be damaged from thermally induced strains during heating and cooling, or they may have temperature limitations occurring below that of the underlying base metal. Additionally, the use of a protective coating increases the expense of employing molybdenum and tungsten in such applications.

It is, therefore, an object of this invention to provide for the use of molybdenum and tungsten and their alloys in the presence of steam at high temperatures.

It is another object of this invention to utilize the inherent advantages of a stable oxide coating formed on these metals under certain conditions.

It is a further object of this invention to limit the oxidizing potential of steam to prevent the formation of the trioxide of molybdenum and tungsten.

It is yet another object of this invention to treat steam in a steam power system with hydrogen.

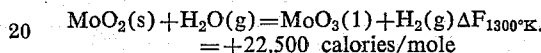
The particular objects of this invention are achieved in one form by introducing a sufficient quantity of hydrogen in a steam atmosphere to prevent the formation of the trioxide of molybdenum or tungsten while, at the same time, permitting the formation of the dioxide. These and other advantages and objects of this invention will be better understood when taken in connection with the following description.

While it has heretofore been mentioned that a limitation in the use of molybdenum and tungsten above 1000° F. is the formation of a volatile trioxide of these metals, the dioxide of these metals provides a stable, protective coating up to temperature of about 1800° F. While it

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has been proposed in the past to operate, for example, a turbine under a reducing atmosphere to prevent oxidation of metal parts, such a solution particularly with respect to steam power generation is very uneconomical. By the teachings of this invention, moderate amounts of a reducing gas, for example, hydrogen may be introduced into a steam system in sufficient quantities only to prevent formation of trioxide, permitting the stable dioxide to be formed. In this manner, the stated deficiencies of molybdenum and tungsten are overcome and these metals may be operated at temperatures up to approximately 1800° F. In the use of hydrogen, thermodynamic considerations lead to the conclusion that molybdenum and its alloys and tungsten and its alloys may be employed without protective coating in a steam atmosphere, by limiting the extent of oxidation by the presence of a low partial pressure of hydrogen. This may be shown as follows:

For the reaction:



then from the relation:

$$\Delta F = -RT \ln \frac{P_{\text{H}_2}}{P_{\text{H}_2\text{O}}}$$

we obtain an equilibrium pressure ratio for 1300° K.

$$\log \frac{P_{\text{H}_2}}{P_{\text{H}_2\text{O}}} = \frac{-22,500}{(2.303)(1.98)(1300)} = 3.80$$

$$\frac{P_{\text{H}_2}}{P_{\text{H}_2\text{O}}} = 1.58 \times 10^{-4} \text{ (at } 1300^\circ \text{K.)}$$

The ratio of concentration is obtained assuming ideal gas behavior:

$$\left[\frac{\text{H}_2}{\text{H}_2\text{O}} \right] = \frac{2}{18} \times 1.58 \times 10^{-4} = 1.76 \times 10^{-5}$$

Thus at about 1800° F. the concentration of hydrogen somewhat above the equilibrium value (two parts per one hundred thousand) should suppress the formation of the volatile trioxide. At lower temperatures the ratio is more favorable. The ratio should be independent of the total pressure since equal volumes are involved as reactants and products.

There are various methods by which hydrogen may be introduced in a steam generating plant. An important factor in the consideration of what method to employ is the cost. Included among the more favorable methods are (1) introducing hydrogen into the system from a high pressure tank source, (2) making additions to the boiler water which, upon reaction form hydrogen, and (3) the electrolytic dissociation of water with release of the evolved hydrogen to the system.

In estimating the cost of the above-mentioned three systems, such cost was considered from an energy consumption standpoint only with the reasoning being that, for example, in the small central station power equipment utilizing a steam turbine, the cost of the system would, over a long period, be small by comparison with operational cost. A suitable high pressure source of hydrogen is a tank supply together with control equipment to meter predetermined quantities. Such a system is usually employed as a recirculating system where the hydrogen is recirculated or recovered.

Various additives may be supplied to the boiler water to produce hydrogen at high temperatures. Examples are aqueous ammonia and various metal hydrides, such as, calcium and sodium.

In electrical power generating systems where a plentiful supply of power is available, hydrogen may be supplied by electrolysis of water. A particular electrolysis system is disclosed and claimed in copending application Serial

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No. 861,968 assigned to the same assignee as the present invention and filed concurrently herewith. In the Smith application, electrolysis is employed in conjunction with the boiler water itself through a boiler water circuit whereby hydrogen is released in the boiler, and oxygen without.

It has been shown, therefore, by this invention that the formation of the trioxides of molybdenum and tungsten may be suppressed to the extent that only the dioxides form and that these dioxides act in the form of a protective coating. It has further been shown that the use of hydrogen as a treatment for steam is an economical process and that the combination, therefore, provides for the use of molybdenum and tungsten when exposed to steam particularly in steam turbines at elevated temperatures and pressures. It is, of course, contemplated that the teachings of this invention may be employed to prevent corrosion of the given metals in steam atmospheres generally or where corrosion may take place in certain atmospheres in addition to those containing water vapor or steam.

While the present invention has been described with reference to particular embodiments, it will be understood that numerous modifications may be made with those skilled in the art without actually departing from this invention. Therefore, we aim in the appended claims to cover all such equivalent variations as come within the true spirit and scope of the foregoing disclosure.

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

1. A method of utilizing a metal taken from the class consisting of molybdenum, tungsten and their alloys at temperatures in excess of about 1000° F. in a steam atmosphere which comprises, providing hydrogen in the atmosphere to which said metal parts are exposed, and

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limiting the quantity of hydrogen to prevent formation of the trioxide of these metals and to permit formation of the dioxide of these metals.

2. In a steam power generating system the method of utilizing a metal taken from the class consisting of molybdenum, tungsten and their alloys, for exposure to said steam at temperatures in excess of about 1000° F. which comprises, introducing hydrogen into said steam, and limiting the amount of hydrogen so as to prevent formation of the trioxide of these metals and to permit formation of the dioxide of these metals.

3. The invention as claimed in claim 2 wherein said hydrogen is formed within the steam power system by additives to the boiler water.

4. The invention as claimed in claim 2 wherein said hydrogen is generated by the electrolytic decomposition of water.

5. The invention as claimed in claim 3 wherein said additive is aqueous ammonia.

References Cited in the file of this patent

UNITED STATES PATENTS

1,581,944	Hausmeister	Apr. 20, 1926
1,783,726	Lappe et al.	Dec. 2, 1930
2,857,297	Moore et al.	Oct. 21, 1958
2,878,554	Long	Mar. 24, 1959

OTHER REFERENCES

RCA TN No. 134,	March 12, 1958.
Dauber: Combustion,	August 1956, pp. 47-56.
Uhlig: Corrosion Handbook,	John Wiley and Sons, Inc., N.Y., pp. 520-521.