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PROCESS FOR PREVENTING OXIDATION OF NUCLEAR REACTOR COOLANT CHANNEL MAGNESIUM SHEATHS

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This invention is concerned with a process for protecting magnesium and its alloys from oxidation at high temperatures.

The oxidation of magnesium and a certain number of its alloys becomes very noticeable from 350° C. upwards and accelerates rapidly as the temperature rises. At 450° C., for example, the metal is quite unusable in dry or moist oxidizing atmospheres or in an atmosphere which is inert but moist, because of its reaction with water vapour.

In order to extend the field of use of magnesium and its alloys so that they may be employed at high temperatures, alterations may be made either to its own composition or to the composition of the corrosive atmosphere by addition of corrosion-inhibiting elements or compounds.

Thus, it has been proposed to introduce carbon dioxide or sulphur dioxide into the atmosphere, but large proportions of these gases are required (of the order of 10%); the use of these processes is also limited to heating for a short time in static atmospheres, for example in metallurgical operations.

It has also been proposed to treat magnesium or its alloys with a boiling caustic soda solution, followed by immersion in a 40% solution of hydrofluoric acid. This process is somewhat difficult to put into practice because of the use of a boiling caustic soda solution. Furthermore, it requires the use of large quantities of the inhibiting solutions, particularly in the case of large pieces. In addition, the protection provided by this process fails after long exposure in a moist medium, because of the hydrolysis of the fluoride formed during immersion in the hydrofluoric acid bath.

Magnesium offers much better resistance to oxidation at high temperatures if it contains a certain proportion of beryllium, which may reach 50 to 100 p.p.m. However, the introduction of beryllium into magnesium is critical and increases grain enlargement when hot, which is prejudicial to the mechanical behaviour of the metal.

According to the present invention, there is provided a process for protecting magnesium and its alloys from oxidation at high temperatures, which comprises introducing into the atmosphere surrounding the magnesium or magnesium-alloy article to be protected, which atmosphere would itself oxidize said article, a small proportion of a vaporized fluorine-containing compound, the proportion of fluorine-containing compound employed being such as to provide at least 2γ of fluorine per litre of oxidizing atmosphere.

The action of the vaporized fluorine-containing compound is to form a durable protective layer containing MgF_2 on the surface of the metal. Suitable proportions of fluorine-containing compound are, for example, such that the latter provides from 2 to 3γ of elemental fluorine per litre of oxidizing atmosphere.

All fluorine-containing compounds which can be vaporized at the prevailing temperature, that is a temperature at which the atmosphere would otherwise oxidize the metal article, and which are readily capable of producing fluorine may be employed. Thus excellent results have been obtained, for example, with hydrofluoric acid, trifluoromethyl benzene and Freons which are defined as fluorinated methane and ethane containing chlorine.

The fluorine-containing compound may be introduced into the oxidizing atmosphere in various ways:

(*a*) By bubbling all or some of the oxidizing atmosphere which comes into contact with the magnesium or magnesium alloy through a dilute solution of hydrofluoric acid; the solution containing, for example, 0.05 gm. molecule per litre, i.e., 0.1% HF, and being at a temperature of, for example 25° C.;

(*b*) By similar bubbling through an aqueous suspension of a water-insoluble compound, such as a Freon;

(*c*) By entraining the vapour of a compound having considerable vapour pressure, such as trifluoromethyl benzene;

(*d*) By directly introducing commercial gaseous hydrofluoric acid or any other gaseous fluorine-containing compound into the oxidizing gas;

(*e*) By hydrolyzing a solid fluoride with the water vapour contained in the oxidizing atmosphere, so as to introduce gaseous hydrofluoric acid into the said atmosphere; hydrolysis being carried out by passing the gas flow over the solid fluoride.

Magnesium and its alloy may be heated up to 500° C. for several hundred hours in an oxidizing atmosphere containing such a fluorine-containing compound without any appreciable oxidation developing, even in the presence of moisture. The proportion of fluorine-containing compound may, moreover, be reduced if the heating temperature is lower.

In addition, if metal which has undergone this treatment is subsequently heated in an oxidizing atmosphere which does not contain such a fluorine-containing compound, the protection lasts for a further several hundred hours. This property imparts great flexibility to the process. Thus, if the system for introducing the fluorine-containing compound breaks down, there is plently of time either to repair the said system or to provide for its replacement, without stopping the gas flow which circulates round the magnesium articles.

Owing to the resistance to oxidation which it provides, use of the method according to the invention enables the temperature at which magnesium articles may be employed to be increased by approximately 150° C.

The protection provided by the process according to the invention lasts in the presence of radiation such as that encountered in nuclear reactors, for example in Marcoule's reactors of type G. 1, in which the fuel is, in fact, sheathed with magnesium cooled by a flow of moist air.

In order that the invention may be more fully understood, the following examples are given by way of illustration only:

Example 1

Tests were made on samples of pure magnesium. The proportions of impurities in the metal were as follows:

	P.p.m.
Fe	530±30
Mn	280±20
Al	100±30
Cu	27±5
Cl	35±20

The samples were mechanically polished with emery paper and then chemically polished with a mixture of 90 parts of ethyl alcohol and 10 parts of nitric acid.

The samples were placed in a graphite tube and heated in an electric oven to 450° C. There was an air flow of 200 cc. per minute through the tube; the air being saturated with moisture at 25° C.

Prior to passing through the tube, the air was bubbled through an aqueous solution of hydrofluoric acid contain-

ing 0.05 gm. molecule per litre and at a temperature of 25° C.; in addition to entraining hydrofluoric acid, this had the effect of simultaneously humidifying the air. The proportion of HF in the gas after bubbling was 2.7 γ/litre.

Corrosion was evaluated by measuring the increase in weight of the samples. The samples were identical and these measurements were therefore comparable.

Oxidation time	2 hours	8 days	15 days	23 days	48 days.
Gain in weight	0	0.9 mg	1 mg	1 mg	1.3 mg.

An identical sample, treated under the same conditions, but in the absence of HF, increased in weight by 16 mg. at the end of 18 hours.

Example 2

A sample was subjected to treatment with a hydrofluoric acid-containing air for 15 days under the same conditions as in Example 1 and was then heated for 30 days under the same conditions as in Example 1, but in the absence of HF. No appreciable corrosion appeared.

Example 3

Tests were carried out on portions of magnesium sheath, 50 cm. in length, for uranium rods for nuclear reactors, externally prepared as before; heating was effected by electrical heater plugs disposed inside the sheaths and was regulated to produce a temperature of 450° C. on the outside of the sheath. The portions of sheath were disposed in a stainless steel duct jacketed with nuclear graphite.

Air was pre-heated to 200° C. and passed through the duct at a velocity of 25 m./second and with a rate of supply of 250 cu. metres/hour. Hydrofluoric acid was introduced into the air, simultaneously with the water vapour required to moisten it, by vaporizing a measured quantity of a solution of hydrofluoric acid.

The tests carried out give results identical with those of Example 1. After a fine protective surface layer had been formed, oxidation was stopped and no corrosion appeared.

We claim:

1. In a method for reducing oxidation in a nuclear reactor wherein a flow of an oxidizing atmosphere is passed over magnesium sheaths containing fissile material,

the steps which consist in bubbling at least a part of the oxidizing atmosphere through a dilute aqueous solution of a compound selected from the group consisting of hydrogen fluoride, fluorinated methane and ethane containing chlorine and trifluoromethyl benzene entraining at least 2×10^{-6} grams of fluorine per liter of the oxidizing atmosphere, then passing the atmosphere containing fluorine over the sheaths and maintaining the atmosphere at temperatures between 250° C. and 500° C. when passed over the magnesium sheaths.

2. In a method for reducing oxidation in a nuclear reactor wherein a flow of an oxidizing atmosphere at temperatures between 350° C. and 500° C. is passed over magnesium sheaths containing fissile material, the steps which consist in bubbling the oxidizing atmosphere through an aqueous solution of about 0.1% hydrogen fluoride per liter maintained at about 25° C. and then passing the atmosphere containing hydrogen fluoride over the sheaths.

3. In a method for reducing oxidation in a nuclear reactor wherein a flow of air is passed over magnesium sheaths containing fissile material, the steps which consist in bubbling at least a part of the air through an aqueous suspension of fluorinated methane and ethane containing chlorine entraining from 2×10^{-6} to 3×10^{-6} grams of the fluorinated methane and ethane containing chlorine per liter of the air, then passing the air containing the fluorinated methane and ethane containing chlorine over the sheaths and maintaining the air at temperatures between 250° C. and 500° C. when passed over the magnesium sheaths.

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