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METHOD OF PREVENTING CARBURIZATION IN MOLTEN METALS

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5 Claims. (Cl. 75—66)

Our invention relates to a method of protecting metals from carburization in liquid metal coolants.

Liquid metals have excellent heat transfer characteristics, and are employed as coolants in industrial processes and in nuclear reactors. The liquid metals will, in service, take up carbon from various sources, such as graphite, hydrocarbons and certain carbon-containing steels. Metal compositions containing carbide-forming elements become carburized and damaged when exposed to carbon-contaminated liquid metals. Heretofore, in order to use stainless steels in sodium systems, elaborate precautions have been necessary to limit the carbon concentration of the sodium. For example, the "Liquid Metals Handbook," Sodium-NaK Supplement (1955), page 177, states:

> "The carburization of stainless steel is a cumulative process, and the total amount of hydrocarbons that can be added to a system during its lifetime must be restricted on the basis of exposed area and allowable depth of carburization. In one application, a total of 0.0002 lb./ft. of exposed steel area has been set as a limit for carbon addition of any kind to the system. Prior removal of trace hydrocarbons from the cover gas is important, since, unlike oxygen, removal during operation is not feasible."

An object of our present invention, therefore, is to provide a method of protecting structural metals from carburization.

Another object is to provide a composition for removing carbon from a liquid metal coolant system.

Another object is to provide a method of protecting alloy steels from carburization in liquid metal systems.

Still another object is to provide a low cost gettering composition for protecting stainless steel from carburization in sodium.

The above and other objects and advantages of our invention will become apparent from the following detailed description taken together with the accompanying claims.

In accordance with our present invention, metals may be protected from carburization in a liquid metal system containing carbon by placing in said system a metal having a low carbon activity.

The materials which may be used in our invention as getters for protecting alloy steels from carburization are those metals which have a lower carbon activity than iron. Metals with low carbon activity have a strong affinity (high driving force) for carbon and form stable carbides relatively rapidly. Iron itself is substantially neutral with respect to carbon in carbon-saturated sodium.

It has been found that the carbon activity level, rather than the carbon concentration, is the controlling factor in carbon diffusion. Thus, between steels initially saturated with respect to carbon, carbon diffuses down an activity gradient even though the diffusion may be uphill with respect to carbon concentration. Hence, the driving force in liquid metal systems is not the carbon concentration gradient but the carbon activity level.

Among the elements with a lower carbon activity than

iron, and which may be satisfactorily used in our invention for carbon gettering, and for protecting alloy steels from carburization, are manganese, chromium, molybdenum, tantalum, vanadium, niobium, and titanium. These elements will preferentially form more stable carbides than iron.

Our gettering compositions operate effectively in all liquid metals and are not limited to use in any single liquid metal or eutectic system. Examples of the liquid metals are sodium, lithium, tin, bismuth, and bismuth-tin.

The foregoing low carbon activity metals may be used singly or in combination for service in gettering carbon and in protecting alloy steels from carburization. We found, however, that surface layers of carbide or oxide form on the pure metal or metal combinations which act as diffusion barriers, and tend to progressively decrease the effectiveness of the gettering action. We have discovered that such effects can be avoided by distributing the gettering element in a diluent material. This allows further diffusion of carbon into the composition, formation of surface carbide diffusion barriers is avoided, and the gettering action is not impaired with the passage of time. As an example of such behavior, we found that chromium metal, which has a very low carbon activity, is not as effective in protecting alloy steel from carburization as is chromium alloy.

The criteria for a satisfactory base or alloying material include a fairly high rate of carbon diffusion therein, solubility for carbon and getter, and a neutral or slightly lower activity relative to carbon. The solubility requirement is important because if a continuous carbide layer is formed on the surface of the getter, we have found that it forms a diffusion barrier to further absorption of carbon, and hence the effectiveness of the getter would rapidly diminish after a short time. Among the practical, commercially-available diluents are iron and nickel; alloys of these metals with the low carbon activity metals comprise useful hot trap carbon getters.

However, even in a diluent material, the effective range of the alloy constituents varies with concentration. Below about 5 weight percent total alloy additive concentration, carbon gettering is low; between about 5–30 weight percent total alloy in either nickel or iron base getters, efficient carbon gettering is achieved; but beyond about 30 weight percent the effectiveness again drops. The drop off beyond 30 weight percent may be due to the formation of undiffusible surface layers of metal carbides, or to the formation of intermetallic compounds which act as a barrier to carbon diffusion to the interior. For example, the effectiveness of chromium alloys as hot trap carbon getters increases with increasing chromium content and then decreases. The optimum chromium range within the 5–30 weight percent range is about 9–12 weight percent, and a very effective alloy is a 9 Cr–1 Mo ferritic steel.

The effective ranges of the low carbon activity metals in iron and nickel base alloys are indicated as follows. The effectiveness and component ranges of our gettering compositions are not significantly influenced by the particular liquid metal from which carbon is being removed, or by the diluent base.

	Weight percent		Weight percent
Cr	0.5–30	Ta	0.5–25
Mn	0.5–15	Ti	0.5–10
Mo	0.5–10	V	0.5–15
Nb	0.5–10		

The alloy constituents, within the above concentration

range for each metal, may be used in any combination in binary, ternary, and quaternary iron or nickel base alloys, provided the total alloy content does not exceed about 30 weight percent. Examples of binary alloys would be any of the foregoing metals in the indicated concentrations in iron or nickel. Examples of ternary and quaternary nickel and iron alloys (weight percent) are as follows:

Ternary Alloys

Cr	0.5–25	Mo	0.5– 5
Mo	0.5– 5	Ta	0.5–15
Cr	0.5–25	Ti	0.5– 5
Ta	0.5–25	V	0.5– 3
Mo	0.5–10	Ta	0.5–15

Remainder essentially Ni

Ternary Alloys

Mo	0.5–10	V	0.5–10
Ta	0.5–20	Ti	0.5– 5
Cr	0.5–20	Ta	0.5–10
Cr	0.5–20	Mo	0.5– 5
V	0.5–10	Ta	0.5–10

Remainder essentially Fe

Quarternary Alloys

Cr	0.5–15	Ta	0.5–10
Mo	0.5– 5	Ta	0.5–10
Cr	0.5–15	Ti	0.5– 3
Cr	0.5–15	Ta	0.5–10
Mn	0.5–15	Ti	0.5– 5
Ti	0.5–10	Ti	0.5– 3
Cr	0.5–15	V	0.5– 3
Mo	0.5– 5	Ti	0.5– 3
Ta	0.5–10	V	0.5– 3
Mo	0.5– 5	V	0.5– 3
Mo	0.5– 5		

Remainder essentially Ni

Quaternary Alloys

Nb	0.5–10	V	0.5– 5
V	0.5–10	Ta	0.5– 5
Mo	0.5–10	Ta	0.5– 5
Cr	0.5–20	Mo	0.5– 5
Ti	0.5–10	Ti	0.5– 3
V	0.5– 5	Mo	0.5– 3
Ta	0.5–10	Mo	0.5– 3
V	0.5– 5		

Remainder essentially Fe

Our gettering material may very satisfactorily be used in a hot trap in an operating liquid metal system. The hot trap would be of conventional design and contain thin sheets or ribbons of the getter in a large surface-to-volume ratio. The material is fabricated in the form of a cartridge which can be inserted and removed from the hot trap. There could be full liquid metal flow through the hot trap, or, more likely, the hot trap would be situated in a bypass loop of the system. The temperature in the hot trap is desirably maintained at a higher temperature than the liquid metal system, for instance about 150–400° F. higher, in order to hasten the rate of reaction with the getter material. In a sodium-cooled nuclear power reactor, the current designs of which operate at peak temperatures of about 1000° F., the side stream hot trap getter would, for example, satisfactorily operate at about 1200° F.

The following examples are offered to illustrate our carbon gettering invention in greater detail. Metal samples 0.060 inch thick were exposed for 200 hours in 1300° F. sodium saturated with carbon. The metals and test results are shown below.

Material (wt. Percent)	Carbon in Alloy before Exposure (wt. Percent)	Carbon in Alloy after Exposure (wt. Percent)
0.5 Cr–0.5 Mo	0.12	0.55–0.64
1.25 Cr–0.5 Mo	0.12	0.90–0.91
2.25 Cr–1 Mo	0.12	1.27–1.35
5 Cr–0.5 Mo	0.10	1.39–1.45
5 Cr–0.5 Mo-Ti	0.08	1.60–1.66
5 Cr–0.5 Mo-Si	0.10	1.01–1.14
7 Cr–0.5 Mo	0.10	1.50–1.64
9 Cr–1 Mo	0.10	1.84
304 stainless steel	0.06	0.72–0.78
12 Cr (410 stainless steel)	0.10	1.50–1.55
17 Cr (430 stainless steel)	0.08	1.58–1.62
50 Cr	0.06	0.07–0.09
Cr	nil	0.04–0.05
Zr	nil	0.05–0.06
12.2 Mn	0.04	1.2
4.5 Mo	0.02	0.9
(Remainder essentially Fe)		
30 Cr	0.03	1.08
21.6 Cr–2.2 Mo	0.07	1.8
11.5 Cr–1.3 Mo–1.1 Ti	0.17	1.1
10.3 Cr–0.5 Mo	0.11	1.6
5 Cr–0.5 Mo–2 Ti	0.09	1.95
2.4 Mo–4.5 Ta–5.1 V	0.03	1.85
(Remainder essentially Ni)		

It should be appreciated that the foregoing examples are illustrative rather than restrictive of our invention. Our invention should be understood, therefore, as being limited only as is indicated in the appended claims.

We claim:

1. A method of preventing carburization of an alloy steel in a hot molten metal system selected from the group consisting of sodium, lithium, tin, bismuth, and bismuth-tin, which comprises placing in said molten metal an alloy consisting essentially of approximately 5–30 weight percent of at least one metal selected from the group consisting of manganese, chromium, molybdenum, tantalum, vanadium, niobium, and titanium, and the remainder at least one metal selected from the group consisting of iron and nickel, thereby gettering carbon from said molten metal in said alloy.

2. The method of claim 1 wherein said first-named metal in said alloy consists of about 9–12 weight percent chromium.

3. The method of claim 1 wherein said alloy is a ferritic steel containing about 9 weight percent chromium and about 1 weight percent molybdenum.

4. The method of claim 1 wherein said alloy, in a form having a high surface area-to-volume ratio, is placed in a hot trap, said trap being maintained at a temperature of about 150–400° F. higher than the portion of said liquid metal system outside of said hot trap.

5. The method of preventing the carburization of an alloy steel structural material in a liquid sodium system containing carbon at a temperature of about 1000° F., which comprises placing a ferritic steel containing about 9 weight percent Cr–1 weight percent Mo in a high surface area-to-volume ratio in a side stream hot trap maintained at a temperature of about 1200° F., and passing said sodium through said hot trap, thereby gettering carbon on said ferritic steel.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,043,680 July 10, 1962

Walter C. Hayes et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, lines 9 to 50, the table should appear as shown below instead of as in the patent:

TERNARY ALLOYS

0.5-25 Cr; 0.5- 5 Mo	Remainder essentially Ni
0.5- 5 Mo; 0.5-15 Ta	
0.5-25 Cr; 0.5- 5 Ti	
0.5-25 Ta; 0.5- 3 V	
0.5-10 Mo; 0.5-15 Ta	

TERNARY ALLOYS

0.5-10 Mo; 0.5-10 V	Remainder essentially Fe
0.5-20 Ta; 0.5- 5 Ti	
0.5-20 Cr; 0.5-10 Ta	
0.5-20 Cr; 0.5- 5 Mo	
0.5-10 V ; 0.5-10 Ta	

QUATERNARY ALLOYS

0.5-15 Cr; 0.5- 5 Mo; 0.5-10 Ta	Remainder essentially Ni
0.5- 5 Mo; 0.5-10 Ta; 0.5- 5 Ti	
0.5-15 Cr; 0.5- 5 Mo; 0.5- 3 Ti	
0.5-15 Cr; 0.5- 5 Mo; 0.5- 3 V	
0.5-15 Mn; 0.5-10 Ta; 0.5- 3 Ti	
0.5-10 Ti; 0.5-10 Ta; 0.5- 3 V	
0.5-15 Cr; 0.5- 3 Ti; 0.5- 3 V	

QUATERNARY ALLOYS

0.5-10 Nb; 0.5- 5 V ; 0.5- 5 Ta	Remainder essentially Fe
0.5-10 V ; 0.5-10 Ta; 0.5- 5 Mo	
0.5-10 Mo; 0.5- 5 V ; 0.5- 3 Ti	
0.5-20 Cr; 0.5- 5 V ; 0.5- 3 Mo	
0.5-10 Ti; 0.5- 5 Ta; 0.5- 3 Mo	

Signed and sealed this 29th day of January 1963.

(SEAL)
Attest:

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