United States Patent [19]

Troy et al.

[11] 3,883,147

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[54] DRY LUBRICATED MATERIALS

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[52] U.S. Cl. .... 277/96 R; 60/39.51; 165/9; 252/12

[51] Int. Cl. F16j 15/34; C10m 7/06; C10m 7/04

[58] Field of Search 252/30, 12, 12.2, 12.4, 252/12.6; 148/6.35; 277/96; 60/39.51; 165/9

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[57] ABSTRACT

Dry lubricated members particularly adapted for use as cold side rubbing seals in the regenerator section of gas turbine engines, the members comprising a substrate with an initial working surface of an iron oxide matrix containing an interspersed mixture of graphite and a trapping material in the form of an inorganic compound such as salt or oxide. Subsequent to a break-in period the work surface and any mating surface therewith both acquire a substantially continuous film of high oriented iron hematite — Fe_2O_3.

10 Claims, 3 Drawing Figures

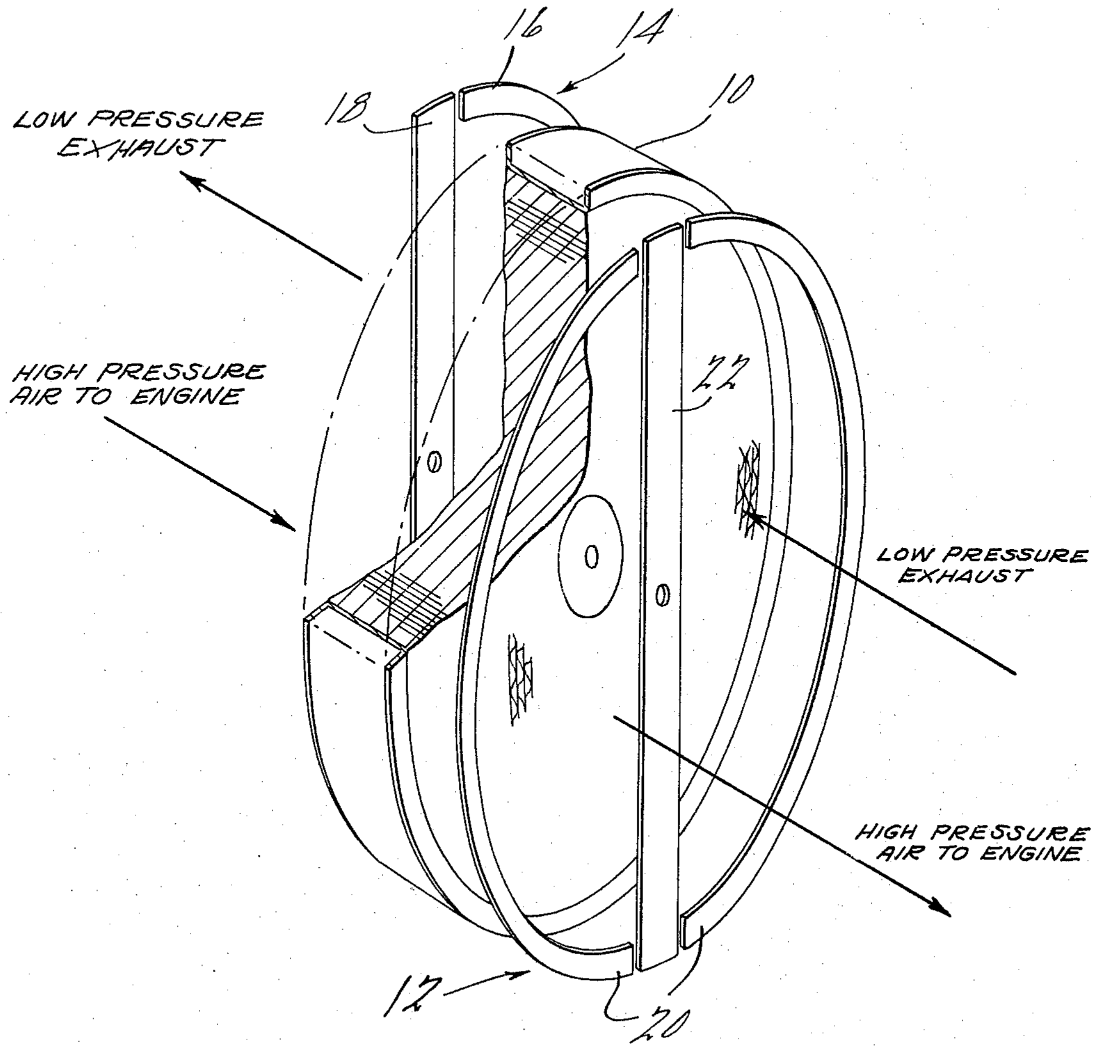

16
14
10
18
LOW PRESSURE EXHAUST
HIGH PRESSURE AIR TO ENGINE
22
LOW PRESSURE EXHAUST
HIGH PRESSURE AIR TO ENGINE
12
20

FIG. 1.

FIG. 2a.

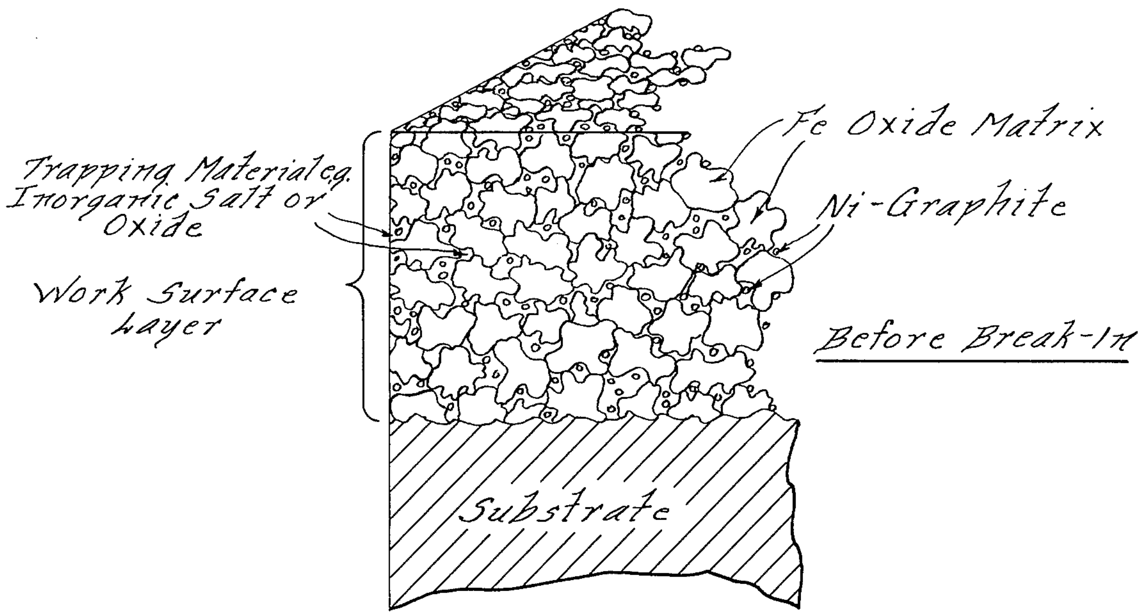
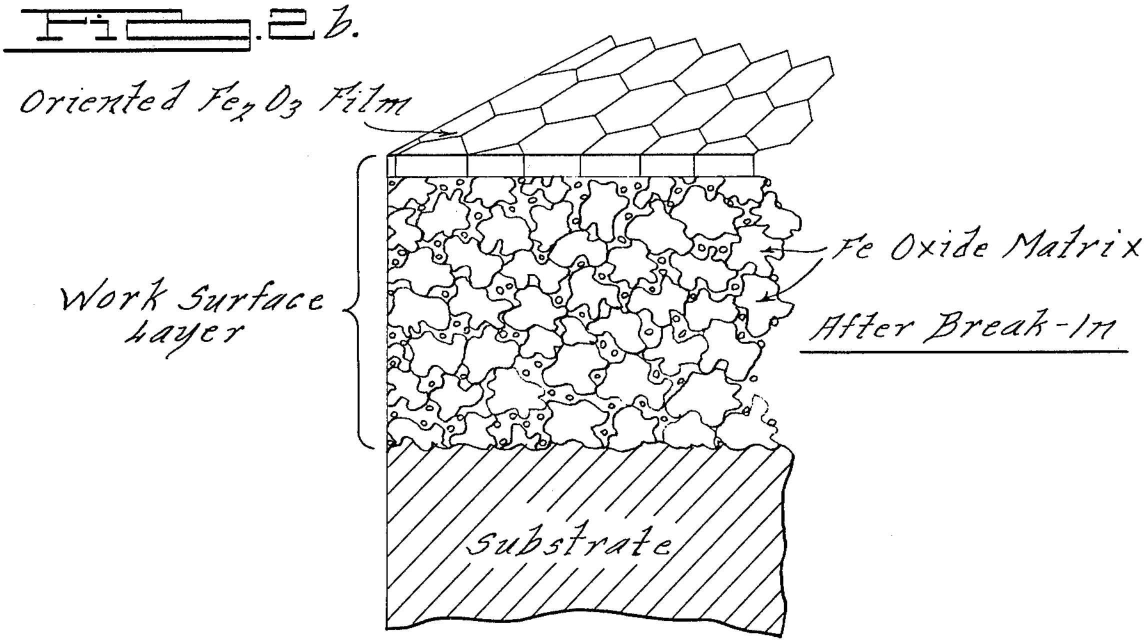

Fe Oxide Matrix
Trapping Material eg. Inorganic Salt or Oxide
Ni-Graphite
Work Surface Layer
Before Break-In
Substrate

FIG. 2b.


Oriented Fe_2O_3 Film
Fe Oxide Matrix
Work Surface Layer
After Break-In
Substrate

DRY LUBRICATED MATERIALS

CROSS REFERENCE TO RELATED APPLICATIONS

This application is related to two co-pending applications filed on even date herewith. The first application Ser. No. 212,249, now abandoned, is entitled: "Iron Oxide Material and Members for Dry Lubricated Systems Including the Method of Preparation Therefor," the inventors being Amedee Roy, Claude Belleau and James M. Geyman. The second application Ser. No. 212,414 now U.S. Pat. No. 3,747,944 is entitled, "Dry Lubricated Materials, Members and Systems with Boron Nitride and Graphite," the inventors being Amedee Roy and James M. Geyman. The co-pending applications are assigned to the same assignee as the present application and the contents thereof are incorporated herein by reference. The invention constitutes an improved variation of the inventions disclosed in the aforementioned co-pending applications.

BACKGROUND OF THE INVENTION

This invention relates generally to low friction rubbing materials for use in dry lubricated systems particularly at temperatures up to the range of about 1000° F. It also relates to methods of preparation for these materials. Dry lubricated systems are those wherein mating surfaces operate in sliding or rubbing contact without a lubricant, such as oil. The invention is especially adapted to provide material and members for use in cold side rubbing seals for the regenerator section of gas turbine engines but will find use in other instances, such as in Wankel engines for example. Abradable seals have been used in applications of the type contemplated herein. However, they have been of the sintered compressed type referred to in the first of the above-referenced co-pending applications.

SUMMARY OF THE INVENTION

By means of this invention a member having an initially abradable work surface, adapted for use against a mating member is formed by providing a matrix work surface layer of iron oxide — wustite FeO, magnetite Fe_3O_4 or hematite Fe_2O_3, or mixtures thereof — on a suitable substrate, such as a metal substrate. The iron oxide matrix contains interspersed in the interstices thereof a mixture of graphite particles and a trapping material in the form of an inorganic compound such as a salt or an oxide. During break-in, such as at the relatively low temperatures to which turbine engine regenerator cold seal members are exposed, it has been found that the incorporation of graphite into the initial iron oxide matrix along with the interstitially interspersed trapping material, provides a material which forms an oriented Fe_2O_3 film on the working surface of the substrate with an improved low friction and wear characteristics afterward. Transfer of the film to the mating surface occurs also. A material is thus provided in general which is particularly adapted for relatively low temperature use under dry lubrication conditions.

Following a suitable rubbing run-in or break-in period against a mating surface, preferably at elevated temperatures generated by frictional heat, an external temperature source or preferably both, the member having this material as its work surface is ready for service use in dry lubricated systems such as those which exist in the cold side of the regenerator section of a gas turbine engine. For example, the break-in may take place in the actual initial operation of the engine regenerator section wherein the cold seal members thereof have been provided with the initial work surfaces according to this invention.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** consists of a schematic drawing of a more or less typical gas turbine engine regenerator system including the various seal systems therefor.

FIGS. **2***a* and **2***b* are fragmentary schematics illustrating the structure of the material according to this invention before and after break-in, respectively.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The regenerator section of a gas turbine engine as shown in FIG. **1** includes inner and outer seal systems **12** and **14** respectively, also known as hot and cold side seal systems, which are positioned on opposite sides of a regenerator core **10.** The cold seal system includes a cold rim member **16** and a cold cross arm member **18.** The hot seal system includes hot rim members **20** and a hot-cross-arm member **22.** The seal members rub against the core as it rotates. The system is of the dry lubricated type and members **16** and **18** of the cold seal system are abradable at least during an initial run-in period.

According to this invention, the cold side seal members will include any suitable substrate such as stainless steel, or other material which is compatible in thermal expansion characteristics etc. with the working surface layer provided herein and which is oxidation and corrosion resistant. For other systems various substrate materials will be found useful. The working surface layer provided is initially of FeO, Fe_2O_3 or Fe_3O_4 treated according to this invention to form a working contact surface i.e., the surface against which a mating member such as regenerator core **10** is intended to rub and contact. The substrate is preferably of a material such as 430, 442 or 446 stainless steel in the case of turbine engine seal systems and the iron oxide is best formed thereon by the flame or plasma spraying of Fe_3O_4 powder as will be described in detail below.

The iron oxide matrix as prepared will contain a mixture of graphite and a trapping material, the latter consisting of one or more inorganic compounds such as the salts and oxides listed below:

$BaSO_4$	Na_2SO_4*
$CdSO_4$	Na_2S*
CaO	Na_2HPO_4*
Ca_2PO_7	ZnS
$CaSO_4$	ZnO_2
$MnSO_4$	TiO_2
CaF_2	$NaBO_2$*
Na_3PO_4*	

*Preferred trapping materials.
Note: The hydrated forms of the compounds may be used.

The general characteristics of a trapping material according to this invention are:

1. It must have a melting point in excess of the maximum service temperature.
2. It must not be substantially abrasive as to the mating surfaces.
3. It must be softer than the particles which are to be trapped.

4. In some cases, as in turbine engines, it should not be corrosive.
5. It is desirable that it be sprayable for flame or plasma spraying.

The mixture of graphite and trapping material may be added to the iron oxide matrix after it has been formed on the substrate. Preferably the graphite mixture will be used in a ratio of about one part graphite to one part trapping material by weight.

When the iron oxide is sprayed as by plasma or flame spraying and subsequently impregnated with the graphite trapping material mixture, it may be mixed with a leachable salt such as NaCl or the like before being sprayed. The leachable salt is washed out later to leave a porous iron oxide matrix which may then be impregnated with the graphite mixture to form a working surface ready for run-in.

An example of such a method of preparation on a stainless steel substrate may include the steps of:

1. sand blasting the substrate surface,
2. flame spraying Fe_3O_4 powder to form a 0.005 inch thick matrix layer on the substrate.
3. flame spraying additional Fe_3O_4 powder to form a 0.010 inch thick layer on the substrate, the Fe_3O_4 powder being mixed with 10-15% by weight NaCl.
4. leaching the NaCl out of the Fe_3O_4 matrix by washing in an aqueous bath.
5. impregnating the matrix with a mixture of 7,110 graphite (so designated by the Speer Carbon Co.) and trapping material such as $Na_2S \cdot 9H_2O$. Impregnation may be accomplished by fusing the salt and simply pouring it over the iron oxide matrix, allowing it to soak into the interstices. Any excess is scraped off and the member may be baked at say 1,200° F. to remove hydrated water.

A most preferred method of forming the complete iron oxide working surface layer including the graphite plus trapping material and one which is more direct, consists in the flame or plasma spraying of FeO, Fe_2O_3 or Fe_3O_4 powder or mixtures thereof along with graphite-trapping material mixture. This procedure avoids the necessity of leaching the iron oxide matrix and impregnating it with the above described mixture. However, in such a procedure, the graphite must be protected. One way is to spray it in the form of "nickel graphite," that is graphite particles coated with nickel. A typical nickel coated graphite composition which is commercially available is 75% Ni — 25% graphite. Otherwise, the graphite is lost during spraying. Other nickel coated graphite of various compositions such as 50–85% Ni; 50–15% graphite may also be used so long as the graphite is protected by the nickel coating during spraying.

Mixtures of Fe_3O_4, nickel coated graphite and Na_2SO_4 or Na_3PO_4 have been flame sprayed to provide desirable working surfaces according to this invention. A specific example of one such mixture is 50% by weight Fe_3O_4 powder, 30% by weight nickel coated graphite (75–25) and 20% by weight Na_2SO_4. Other examples are:

70% Fe_3O_4
20% Nicoated-Graphite
10% Na_2SO_4

20% Fe_3O_4
45% Nicoated-Graphite
35% Na_2SO_4

50% Fe_3O_4

60% Fe_3O_4
35% Nicoated-Graphite
5% Na_2SO_4

60% Fe_3O_4
20% Nicoated-Graphite
20% Na_3PO_4

-Continued

30% Nicoated-Graphite
20% Na_3PO_4

Thicknesses of 0.010 – 0.030 inches for the working surface layer material prepared according to the above various procedures have been found useful for gas turbine engine application in regenerator sections. Other thicknesses will be useful for other applications. Thickness per se is not critical.

The results of the run-in or break-in of the materials described above have been determined under conditions of actual turbine engine use as for example making regenerator members such as cold cross arms and cold seal rims and incorporating them into an engine regenerator section for break-in during actual operation of the engine. These results indicate that iron oxide matrix particles abrade along with other miscellaneous debris and embed themselves in the trapping material. The iron oxide particles transform to Fe_2O_3 and orient themselves along a crystallographic direction that has the lowest friction i.e., the basal planes of the hexagonal crystal structure of the particles are positioned parallel to the contact surfaces. Sintering occurs between these particles, particularly at engine operating temperatures, to form a substantially continuous surface of Fe_2O_3.

Iron oxide particles with trapping material are also transferred to the mating surface where the Fe_2O_3 cells orient themselves and sinter together in the same manner described above. Although the work surface layers contain iron oxide of various forms initially, it transforms, particularly under elevated temperatures and oxidizing conditions, to Fe_2O_3 which forms a substantially continuous highly oriented film due to the embedding and sintering action.

Run-in or break-in may occur in these materials under a wide variety of conditions. The following schedule shows a few of the conditions which may be used if a member carrying a working surface layer of the material according to this invention is intended to form a part for the regenerator system of a gas turbine engine. These conditions are those which occur in an actual operating gas turbine engine and many such members have undergone break-in in an engine under these actual operating conditions.

SCHEDULES

Running Time, Sched. "A"	Fixture Mins. Sched. "B"	Conditions P_3''	T_3°F.	T_8°F.
15	30	10.7	130	600
15	30	16.6	130	950
15	30	25.7	450	1200
15	30	38.8	450	1200
15	30	55.5	450	1275
15	30	78.5	450	1350
120	120	94.	450	1350

Engine

SCHEDULE "H":

1. 1 hour at idle (23,000–24,000 rpm)	T_8 - 900 to 950° F.
2. 1 hour at 70% speed while matching	T_8 - 1120 to 1150 to 1200° F.
3. 1 hour at 80% speed	T_8 - 1200° F.
4. 15 minutes at 90% speed	T_8 - 1200° F.
5. 15 minutes at 95% speed	T_8 - 1200° F.
6. 15 minutes at 97½% speed	T_8 - 1200° F.

-Continued

	Engine
SCHEDULE "H":	
7. 15 minutes at 97½% speed	T_8 – 1275° F.
8. 15 minutes at 97½% speed	T_8 – 1350° F.

SCHEDULE CONDITIONS DEFINED

P_3''	= pressure in inches of Hg of cold gas entering regenerator as indicated in FIG. 1.
T_3° F.	= temperature of the cold face of the regenerator as at the outer seal system of the regenerator of FIG. 1.
T_8° F.	= temperature of the hot face of the regenerator as at the inner seal system of the regenerator of FIG. 1.

Having described the invention, it is to be defined according to the following claims in which exclusive rights are set forth.

What is claimed is:

1. A member for use under dry lubricated conditions comprising: a substrate having a working surface thereon comprised initially of an iron oxide matrix containing an interspersed mixture of a trapping material means for embedding abraded particles and debris particularly iron oxide particles in the work surface during use selected from the group consisting of barium sulfate, cadmium sulfate, calcium oxide, calcium phosphate, calcium sulfate, manganese sulfate, sodium phosphate, sodium sulfate, sodium sulfide, sodium biphosphate, zinc sulfide, zinc oxide, titanium oxide, calcium fluoride, sodium borate, and mixtures thereof and a component selected from the group consisting of nickel coated graphite, graphite and mixtures thereof.

2. The member of claim **1** wherein the interspersed mixture is trapping material and graphite, present in about a proportion of **1:1** by weight.

3. The member of claim **1** wherein the trapping material is selected from the group consisting of Na_2SO_4, Na_2S, $NaHPO_4$, Na_3PO_4, $NaBO_2$ and mixtures thereof.

4. The member of claim **1** wherein the substrate is a stainless steel.

5. The member according to claim **1** wherein the initial working surface comprises a matrix consisting substantially of Fe_3O_4 and the interspersed mixture is nickel coated graphite and a trapping material selected from the group consisting of Na_2SO_4, Na_2S, $NaHPO_4$, $NaBO_2$ and mixtures thereof.

6. The member according to claim **5** wherein the proportions of the various components of the working surface are about **50%** by weight Fe_3O_4, **30%** by weight nickel coated graphite and **20%** by weight trapping material.

7. A regenerator section for a gas turbine engine comprising at least two members arranged for rubbing contact during operation of the engine, one of the members having an initial working surface comprised of an iron oxide matrix containing an interspersed mixture of nickel coated graphite or graphite and a particle-debris trapping material selected from the group consisting of barium sulphate, cadmium sulphate, calcium oxide, calcium phosphate, calcium sulphate, manganese sulphate, sodium phosphate, sodium sulfate, sodium sulfide, sodium biphosphate, zinc sulfide, zinc oxide, titanium oxide, calcium fluoride, sodium borate, and mixtures thereof, and wherein a transformation occurs in the work surface during a break-in period, forming as a result, a substantially continuous highly oriented film of Fe_2O_3 on the work surface of the one member and a film of Fe_2O_3 is also formed on the mating second member by transfer from the one member to the second member.

8. The article of claim **7** wherein the one member is selected from the group consisting of regenerator seal rims and cross-arms, the mating surface being provided by the regenerator core.

9. The article according to claim **7** wherein the initial working surface is comprised of an Fe_3O_4 matrix.

10. The member according to claim **1** wherein the graphite used is nickel coated graphite.

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