

1

3,370,006 BEARINGS

Charles Campbell, Thames Ditton, England, assignor to Morganite Research and Development Limited, London, England, a corporation of England
No Drawing. Filed Nov. 2, 1964, Ser. No. 408,366
Claims priority, application Great Britain, Nov. 6, 1963, 43,832/63
6 Claims. (Cl. 252-12)

This invention relates to an anti-friction composition, anti-friction elements made therefrom, and to bearings and bearing assemblies including such elements.

Applicants have developed the use of nickel oxide and/or cobalt oxide in bearing surfaces in order to obtain excellent lubrication and wear resistance at high temperatures. It is found that these oxides form a patina on the bearing surface and it is believed that this patina provides the anti-friction properties.

It has now been found however that, for some reason which is not clear, the nickel or cobalt oxide are prone to an undue amount of wear below about 600° C. This is a substantial disadvantage since, although the nickel or cobalt oxides are designed for use with high temperature engines and the like, such engines must pass through the lower temperature ranges during starting up; it is then that the nickel oxide or cobalt oxide, and hence the bearing, is liable to be subjected to excessive wear.

According to the present invention there is provided an anti-friction composition containing nickel oxide and/or cobalt oxide together with a less wear-resistant, high melting (i.e. above 700° C.) solid lubricant which is non-reducing at high temperatures. The requirement that the solid lubricant must be non-reducing at high temperatures is set by the need to ensure that there is no extensive reduction of the nickel oxide or cobalt oxide during use.

The melting point of the solid lubricant must be above 700° C. and may have to be higher depending on the use to which the anti-friction composition is put. It will be clear that the melting point must always be higher than any temperature that the composition may reach during use.

Examples of solid lubricants that have been found effective include Group IIa fluorides, phosphates and borates, e.g., $Mg_2P_2O_7$, MgF_2 , $Ca_3P_2O_7$, CaB_4O_7 and BaF_2 . Also found to be effective is lead monoxide. A particularly preferred solid lubricant is calcium fluoride which is found to operate as a lubricant at temperatures up to 900° C., and it is particularly efficient over the range 200°-600° C. The solid lubricant is preferably used in amounts of at least 5% by weight of the anti-friction composition preferably 8-15% by weight of the composition. Suitably up to 25% by weight of the composition is present.

As stated above, the prime advantage of these solid lubricant additives lies in the provision of wear-resistant properties at temperatures below 600° C. They nevertheless also help in providing lubricating properties at higher temperatures.

Provided the anti-friction element is to be used in an oxidizing atmosphere, part of the cobalt or nickel oxides may be replaced by cobalt or nickel metal, which metal is then gradually oxidized in situ. There must, however, be sufficient of these oxides present initially at the bearing surface to ensure that the element provides lubrication immediately on attaining the high temperatures, e.g.,

2

at least 30% of the bearing surface being the oxide. The oxidation in situ of the metal must be sufficient to replace continuously the oxide patina as it is worn away.

It has been found desirable for some purposes to include in the anti-friction composition oxides which form eutectic mixtures with nickel and/or cobalt oxide. Examples of these are aluminium, magnesium, zinc and stannic oxides and titanium dioxide, and mixtures of these. The prime advantage in including these oxides is that they form a eutectic with all or some of the nickel oxide and/or cobalt oxide, depending on the quantity added, and thus reduce the temperatures required for sintering or other coating processes.

To prepare a mix of the various components of the anti-friction composition, both ball milling and dry blending have been found suitable.

The anti-friction composition may be formed into anti-friction elements providing bearing surfaces. Thus the composition may be used to provide the bearing surfaces in a bearing assembly incorporating a plurality of elements bearing against one another.

Preparation of the anti-friction elements may be by any suitable method, the most preferred being by sintering or flame-spraying the aforesaid composition on to a suitable substrate. Other methods available include bonding of the composition on to the substrate in an enamel, as disclosed in our pending British patent application No. 9,745/63. The bearing surfaces may be applied directly to the substrates, or an intermediate undercoat may be used as desired.

The substrates used for the bearings may be chosen to provide the optimum mechanical and other properties. So far as possible it should be arranged that the coefficient of expansion of the substrate and that of the bearing surface are substantially the same.

It has been found that bearings using the anti-friction composition of the present invention work almost equally effectively over the entire temperature range 20°-1000° C.

It is foreseen that bearing surfaces prepared from the anti-friction composition of the present invention will have many applications, among which may be mentioned the "Cercor" (honeycomb ceramic) heat exchanger ("Cercor" is a trademark) and rotary piston internal combustion engines of the "Wankel" type.

The invention illustrated in the following examples.

Example 1

A mix was prepared containing:	Gms.
Green nickel oxide -----	900
Calcium fluoride -----	100

The above quantities were weighed out and milled dry for 6 hours in a 10" diameter rubber lined ball mill at 60 r.p.m. with 1 kg. of 1" alumina cretoids.

The milled material was passed through a 100 mesh B.S. sieve and transferred to a "Z" bladed mixer. About 200 gm. of an extrusion binder was then mixed in to produce an extrudable composition. The extrusion binder used was that sold under the trademark "Cellofas." This binds the particulate material together during shaping and handling, but decomposes during firing so that only the original components remain.

Rods were extruded from the composition prepared as above, and sintered by firing to 1440° C. in an air atmosphere.

3

Coatings of the material were then applied to a stainless steel substrate with an undercoat of a nickel-chromium alloy by flame-spraying by the "Rokide" (trademark) process.

Bearings obtained by this method were used in a "Cercor" heat exchanger. At 600° C., 100 ft./min., 10 lbs. load, wear rates of 0.00003" per hour were recorded.

Example 2

A mix was prepared containing:

	Gms.
Green nickel oxide (200 B.S. mesh) -----	750
Calcium flouride (300 B.S. mesh) -----	250

The powders were intimately mixed by dry blending, and then flame-sprayed on to a substrate prepared in the normal manner.

Instead of flame-spraying the powders directly after mixing, they may be pressed into blocks and sintered at 1250° C. Following the sintering they are then crushed and sieved through 200 B.S. mesh on to 300 B.S. mesh, and subsequently frame-syrayed as above.

Example 3

A further mix was prepared containing:

	Gms.
Green nickel oxide (200 B.S. mesh) -----	950
Lead oxide (PbO) (300 B.S. mesh) -----	50

The powders were mixed by dry blending and flame-sprayed on to a substrate as in Example 2. In this case sintering was carried out at 1500° C.

Bearing surfaces prepared from this mix had good running properties over a wide range of temperatures. They were also found to have a smaller coefficient of expansion than the mix of Example 2.

Example 4

The wear rate of bearings made according to this invention was measured by forming a $\frac{3}{8}$ " diameter pad of bearing material, and holding it in sliding contact with the underneath stellite-coated surface of a counterface rotating about a vertical axis. The wear-rate was determined by observing the weight loss per hour of the bearing material, and converting this figure into the mean thickness of the material having the same weight as that lost. The tests were carried out with a predetermined pressure between the pad of bearing material and the counterface, i.e., a predetermined bearing load, and the apparatus was contained in a heated chamber. The results of the experiments are tabulated below:

TABLE 1

Material	Test No.	Temp., ° C.	Bearing load, p.s.i.	Surface speed, ft. p.m.	Counterface	Wear-rate, 10 ⁻³ in./hr.
NiO -----	-----	400	60	25	A	0.3
65% wt. NiO and	1	400	60	25	A	0.49
35% wt. CaF ₂ .	2	400	60	25	B	0.45
90% wt. NiO and	1	400	60	25	A	0.09
10% wt. CaF ₂ .	2	400	60	25	B	0.06

Examples 5-9

Bearings of the following compositions were run at 700° C. against a stainless steel EN 54 shaft at a load of 200 p.s.i. and a linear speed of 5 ft./min. for 20 hours, after which time there was found to be no significant wear of the bearing or shaft in any instance. All percentages in these examples are by weight.

Example 5

	Percent
NiO -----	50
CoO -----	40
CaF ₂ -----	10

4

Example 6

	Percent
NiO -----	90
Mg ₂ P ₂ O ₇ -----	10

Example 7

	Percent
CoO -----	85
PbO -----	15

Example 8

	Percent
NiO -----	90
CaB ₄ O ₇ -----	10

Example 9

	Percent
CoO -----	85
CaF ₂ -----	15

What is claimed is:

1. A wear-resistant element comprising a composition flame-sprayed onto a substrate, said composition consisting essentially of at least one oxide selected from the group consisting of nickel oxide and cobalt oxide, together with a material selected from the group consisting of lead monoxide, and fluorides, phosphates and borates of Group IIa metals in an amount of from 5 to 25% by weight of the composition.

2. A wear-resistant element comprising a composition flame sprayed onto a substrate, said composition consisting essentially of at least one oxide selected from the group consisting of nickel oxide and cobalt oxide, together with a material selected from the group consisting of magnesium pyrophosphate, calcium pyrophosphate, calcium pyroborate, magnesium fluoride and barium fluoride in an amount of from 5 to 25% by weight of the composition.

3. A wear-resistant element comprising a composition flame-sprayed onto a substrate, said composition consisting essentially of at least one oxide selected from the group consisting of nickel oxide and cobalt oxide, together with calcium fluoride in an amount of from 5 to 25% by weight of the composition.

4. A wear-resistant element comprising a composition flame-sprayed onto a substrate, said composition consisting essentially of (1) at least one first oxide selected from the group consisting of nickel oxide and cobalt oxide,

(2) a material selected from the group consisting of lead monoxide and fluorides, phosphates and borates of Group IIa metals in an amount of from 5 to 25% by weight of the composition, and (3) at least one second oxide selected from the group consisting of aluminum oxide, magnesium oxide, zinc oxide, stannic oxide and titanium dioxide, the first and second oxides being present in substantially eutectic proportions.

5. A wear-resistant element comprising a composition flame-sprayed onto a substrate, said composition consisting essentially of (1) at least one oxide selected from the group consisting of nickel oxide and cobalt oxide in an amount of at least 30% by weight of the composition,

(2) at least one metal selected from the group consisting of nickel and cobalt in an amount ranging from a trace up to 65% by weight of the composition, and (3) a material selected from the group consisting of lead monoxide, and fluorides, phosphates and borates of Group 5 IIa metals in an amount of from 5 to 25% by weight of the composition.

6. The wear-resistant element of claim 4 wherein said material is calcium fluoride.

References Cited

UNITED STATES PATENTS

3,122,505	2/1964	Rulon-Miller et al.	252—12
3,125,519	3/1964	Graue et al.	252—12
3,297,571	1/1967	Bonis	252—12

DANIEL E. WYMAN, *Primary Examiner*.

I. VAUGHN, *Assistant Examiner*.