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(54) Title: PUMPS FOR HOT AND CORROSIVE FLUIDS

(57) Abrégé/Abstract:
A pump for pumping molten metal or molten salt, said pump comprising at least one component manufactured of a substrate and coated with one or more wear and erosion resistant surface layers,wherein said substrate is provided with at least one intermediate binding layer and one outer layer, and said outer layer comprises at least one refractory oxide.

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(54) Title: PUMPS FOR HOT AND CORROSIVE FLUIDS

(57) Abstract: A pump for pumping molten metal or molten salt, said pump comprising at least one component manufactured of a substrate and coated with one or more wear and erosion resistant surface layers,wherein said substrate is provided with at least one intermediate binding layer and one outer layer, and said outer layer comprises at least one refractory oxide.

Pumps for hot and corrosive fluids

TECHNICAL FIELD

[001] The present disclosure relates to mechanical pumps for pumping hot, corrosive and erosive fluids like liquid metals and molten salts. The pumps can be of any construction or mechanism of operation, such as radial/centrifugal or axial, wherein at least one component is in contact with the liquid metal or molten salt.

BACKGROUND

[002] The effective service life time of conventional mechanical pumps for liquid metals, normally made of iron base alloys, is typically only a few months or perhaps somewhat longer for molten salt pumps, depending on type of metal or salt and operating temperature.

[003] Ceramic pumps or ceramic impellers that may have excellent corrosion and erosion resistance are known in the art, for example through US 3,776,660 and US 6,019,576. Suggested ceramic materials include graphite and silicon carbide, as disclosed for example in US 5,586,863. However, ceramic materials are mechanically sensitive and break easily when subjected to stress. For instance the fracture toughness of ceramic materials including graphite is generally considered to be too low for use as pump components.

[004] Electro magnetic pump technologies have received a lot of interest in the nuclear industry. A NASA technical report, Liquid-Metal Pump Technologies for Nuclear Surface Power (NASA/TM-2007-214851) gives a review thereof. However, the use of electro-magnetic pumps for liquid metals is disadvantageous due to their poor efficiency.

[005] Pumps for liquid metals and molten salts are used in metallurgical industry, metal coating industry and in chemical industry as well. Additionally there is a growing market for new energy production techniques using liquid metal or molten salts as an energy carrier and/or coolant, such as in liquid metal nuclear reactors,

concentrated solar power plants (CSP) and in fusion reactors. Additionally, molten salts are also used for storage of thermal energy.

[006] The pumps have shown to be a critical component in such nuclear or solar power plants since the overall energy efficiency is dependent on the maximum allowed fluid temperature and flow rate. Today, the maximum operating temperature and choice of fluid is basically limited by corrosion and erosion problems of the pump components. Temperatures of the liquid metals and molten salts used for energy production are typically in the range 200-500 °C but it is desirable to go higher in the future, possibly up to 800 °C.

SUMMARY

[007] One object of the present disclosure is to provide a pump for hot and corrosive fluids wherein the pump has an extended service life.

[008] A particular object is to provide a pump for molten lead or lead bismuth eutectic (LBE) for use in nuclear reactors.

[009] This and other objects are achieved by the aspects and embodiments defined in the independent claims. Further advantageous embodiments have been specified in the dependent claims.

[010] A first aspect is a pump for pumping molten metal or molten salt, said pump comprising at least one component manufactured of a substrate and coated with one or more wear and erosion resistant surface layers, wherein said substrate is provided with at least one intermediate binding layer and one outer layer, and said outer layer comprises at least one refractory oxide.

[011] According to an embodiment of said first aspect, the thickness of the surface coating is 0.2 μm to 1000 μm. Preferably the thickness of the surface coating is 5 - 600 μm.

[012] According to a further embodiment, freely combinable with the above aspect and embodiments, the intermediate binding layer comprises at least one layer of TiN, preferably having a thickness of 0.1 - 5 μm.

[013] According to an embodiment, the substrate is a cemented carbide and the refractory oxide outer layer comprises at least 90 % Al_2O_3. Preferably the outer layer comprises at least 99 % Al_2O_3.

[014] According to yet another embodiment, freely combinable with the above, the cemented carbide comprises at least 80 % WC and a metallic binder, said metallic binder comprising at least one metal selected from the group of Co, Ni, Fe, Cr, Al, Mn, Mo, V, Ti, Ta, Zr and Nb.

[015] According to yet another embodiment, freely combinable with the above, said metallic binder comprises Co and/or Fe and/or Ni and/or Cr and/or Mo in combination with Al. Preferably the binder is a Fe-Al, Ni-Al or a Ni-Cr-Mo-Al binder.

[016] A second aspect relates to a pump for pumping molten metal or molten salt, said pump comprising at least one component manufactured of a substrate and coated with one or more wear and erosion resistant surface layers, wherein said substrate is provided with at least one intermediate binding layer and one outer layer, and said outer layer comprises at least one refractory oxide, wherein the substrate is a nickel based alloy comprising at least 30 wt. % Ni, the outer layer comprises a refractory oxide based on ZrO2, preferably yttria-stabilized zirconia (YSZ), and the intermediate metallic binding layer comprises at least of one metal selected from the group Fe, Ni, Co, Cr or Al.

[017] According to an embodiment of said second aspect, the thickness of the surface coating is 0.2 µm to 1000 µm. The thickness of the surface coating is preferably 5 - 600 µm.

[018] Further aspects and embodiments thereof will become apparent to a skilled person upon study of the detailed description and the comparative example.

DETAILED DESCRIPTION

[019] Before the present invention is described, it is to be understood that the terminology employed herein is used for the purpose of describing particular embodiments only and is not intended to be limiting, since the scope of the invention will be limited only by the appended claims and equivalents thereof.

[020] It must be noted that, as used in this specification and appended claims, the singular forms “a”, “an” and “the” also include plural referents unless the context clearly dictates otherwise.

[021] The present disclosure offers a solution to the shortcomings associated with mechanical pumps, mainly erosion and corrosion problems, when using high temperature fluids as energy carrier, energy storage and coolants for future energy production techniques as well as extending the service life time of pumps for the metallurgical industry etc.

[022] By using a metallic substrate, a cermet or a cemented carbide substrate with a metallic binder phase which has good mechanical properties in combination with corrosion and erosion resistant coatings, which are sufficiently well matched regarding thermal expansion, thus enabling good coating adherence, it is possible to construct a mechanical pump for hot fluids with excellent service life time.

[023] The outer surface layer must be hard enough to possess good erosion resistance. Among oxides, the better quality of alumina has 9 out of 10 on the Mohs hardness scale of abrasives and zirconia has a hardness of 8. Alumina and zirconia exhibit good corrosion resistance in for instance liquid lead and LBE. In general, these oxides are suitable for use when pumping a variety of different liquid metals and molten salts of technical interest.

[024] In the same manner alumina has been shown to be highly corrosion resistant in sulphate, nitrate and carbonate molten salts of interest, as an example, for use in concentrated solar power (CSP) applications. Examples of technically interesting salts include, but are not limited to, sodium and potassium nitrates (Na, K)NO3 and lithium, sodium and potassium carbonates (Li,Na,K)CO3.

[025] Several carbides and nitrides such as WC, TiC, B_4C, SiC, TaC, ZrC, TiN, ZrN, BN and carbo-nitrides such as TiCN and TiAlN have a Mohs hardness of 8.5-9.8 and exhibit good erosion resistance and possess sufficiently good high temperature oxidation and corrosion resistance in most of the liquid metals and molten salts of interest for the different industrial applications. For instance, TiC and ZrC have been tested in liquid Pb, Na and Li around 800°C and showed good resistance. However, the adherence of such layers is generally not sufficient for pump components exposed to fluids with high flow rates. For more demanding pump applications, such

as in nuclear reactors, it is necessary to provide an additional outer oxide coating, preferably based on alumina or zirconia.

[026] In the same manner alumina has been shown to be most resistant in molten salts such as potassium and sodium nitrates used for example in concentrated solar power systems (CSP).

[027] In order to achieve perfect growth of an outer protective alumina scale by chemical vapour deposition (CVD) or physical vapour deposition (PVD) it is required to first provide an intermediate layer of a nitride or carbide to promote the ideal oxide structure, TiN, TiC, ZrC, TiCN or mixtures thereof, however preferably TiN. The substrate metal should have a thermal expansion coefficient that is sufficiently close to the coating or coatings, i.e. in the case of alumina as an outer coating, the substrate could preferably be cemented carbide with a metallic binder.

[028] Yttria-stabilized zirconia (YSZ), could for example be used on iron and nickel base alloy substrates since these have more similar thermal expansion coefficients. Suitable techniques to apply YSZ or Thermal Barrier Coatings (TBC) on a metal substrate are Electron Beam Physical Vapor Deposition (EBPVD), Air Plasma Spray (APS), High Velocity Oxygen Fuel (HVOF), Electrostatic Spray Assisted Vapour Deposition (ESAVD) or Direct Vapor Deposition.

[029] YSZ can also be applied directly on a metal substrate but the use of a metallic and/or oxide binding layer (bond coat) as an intermediate layer should be applied before the outer YSZ-layer is deposited. Such a metallic bond coat, Fe- or Ni-based, should preferably contain chromium and some per cent aluminium in order to form a thin alumina scale for optimal adhesion of the outer YSZ-layer.

[030] A pump for hot and corrosive fluids according to aspects and embodiments of the present disclosure comprises at least one component coated with one or more wear and erosion resistant surface layers. This component can be an impeller vane, an impeller or a part of or the entire inner surface of the pump housing. The impeller is he most important part since it is subjected to high flow rates.

[031] The substrate material may be selected from the following group of materials: steels, stainless steels, nickel-, cobalt-, molybdenum-, tantalum- and tungsten-based alloys, cermets and cemented carbides. A material of particular

interest is tungsten carbide, which can be without a binder, or include a metallic binder.

[032] The binder can comprise at least on metal selected from the group of Co, Ni, Fe, Cr, Al, Mn, Mo V, Ti, Ta, Zr and Nb. According to a preferred embodiment the binder is chosen with respect to its stability in liquid lead and LBE at high temperatures and at low oxygen potentials.

[033] The surface coating comprises at least one layer of oxides, nitrides and carbides or mixtures thereof, preferably the coating comprises at least two layers wherein the carbides and/or nitrides comprises at least one element selected from Zr, Ti, Ta, V, Hf, Nb, W, B, Mo, Cr, Al, and Si and/or the oxides comprises aluminium oxide and zirconium oxide and stabilized or doped oxides thereof.

[034] The total thickness of the surface coating is 0.2 µm to 1000 µm depending on the selected coating materials and application techniques. CVD coatings typically have a thickness of about 1 to about 20 µm and APS coatings typically have a thickness of about 50 to about 600 µm.

[035] In a preferred embodiment, the pump comprises an impeller or at least one impeller vane made of a nickel-based alloy provided with a coating comprising one outer layer of yttria stabilized zirconia (YSZ).

[036] Another preferred embodiment comprises of an impeller or at least one impeller vane wherein the substrate is a cemented carbide and the coating comprises at least one intermediate layer, preferably TiN, and, optionally, at least one layer of Al_2O_3. Preferably, the cemented carbide comprises at least 80 % WC and a metallic binder, the metallic binder comprising at least on metal selected from the group of Co, Ni, Fe, Cr, Al, Mn, Mo, V, Ti, Ta, Zr and Nb. The binder is chosen from Fe, Ni, Cr, Mo and Al, preferably the binder contains an amount of Al such that it easily can form aluminium oxide if the surface coating should be damaged.

[037] A particular use of the coated cemented carbide is the use as a structural material for at least one pump component in a pump for pumping liquid lead or LBE, in particular in a nuclear reactor, wherein the liquid lead or LBE has an oxygen concentration below the lead oxide formation limit.

[038] Another use is the pumping of molten salts, such as carbonate, nitrate and sulphate salts for use in energy applications such as CSP.

[039] A nickel-based alloy comprising an outer layer of yttria-stabilized zirconia (YSZ) is also a suitable material for the above uses.

EXAMPLE 1

[040] In the present example a laboratory-screening test of seven different materials were conducted in flowing lead, which simulates the erosive and corrosive environment a pump component would be exposed to in a liquid heavy metal. The materials and material combinations that were tested are presented in Table 1 below.

Table 1. Material samples subjected to comparative erosion and corrosion test

No.	Description
1	Uncoated carbon steel
2	Uncoated austenitic stainless steel
3	Uncoated Kanthal APMT FeCrAl alloy
4	Pre-oxidized Kanthal APMT FeCrAl alloy, i.e. with a thin *in–situ* formed alumina scale
5	Commercial cemented carbide TiN coated tungsten carbide (WC + 6% Co)
6	Commercial Al_2O_3 (ceramic)
7	Commercial thermal barrier coating (TBC) coated nickel-based alloy. Substrate, Haynes 230, air plasma spray (APS) coated with 360 µm yttria stabilized zirconia (YSZ) (ZrO_2 with 7% Y_2O_3) as a topcoat and 150 µm intermediate binder coating comprising of Ni-Co-Cr-Al-Y.

[041] An erosion test facility was constructed by the inventors. In the erosion test facility, housing up to 10 kg of lead, a theoretical flow rate up to 10 m/s could be achieved by rotating the liquid metal using a rotating disk with a diameter of 15 cm. The disk, immersed into the liquid metal, was rotated using an electric motor coupled to the disk using a stainless steel shaft. Air ingress was reduced to a minimum using standard vacuum copper sealing, and the amount of dissolved oxygen in the liquid lead was controlled by means of an Ar-H2-H2O gas mixture. The test samples were placed close to the periphery of the rotating disk, where the highest flow rates were expected. The facility was heated using a 1000 W band heater mounted on the outside of facility and the temperature was controlled using thermocouples of type K and a PID regulator. The test conditions are shown in Table 2.

Table 2. Test conditions	
Amount of lead	10 kg (approximately 1 dm^3)
Flow rate (theoretical)	7 m/s
Temperature	550°C
Oxygen concentration	10^{-7} weight-%
Exposure time	300 h

[042] The samples were removed after 300 h and post-exposure examination was carried out using a standard optical microscope reaching magnifications up to about 1000x. The tested materials were evaluated with respect to before and after appearance, color and erosion cavitation, as well as from the amount of lead attached to the sample, i.e. wettability.

[043] The screening test revealed large differences in erosion and corrosion resistance between the tested specimens. The uncoated steel samples 1 – 3 showed severe erosion and corrosion damage, meaning a noticeable shift in appearance from smooth metallic surfaces to dark uneven and notched surfaces. The least

damage was found on the uncoated FeCrAl alloy, sample 3. The coated samples, including the pre-oxidized FeCrAl alloy, sample 4, showed no or little damage.

[044] Sample 6, the commercial Al_2O_3-ceramic and sample 7, the YSZ coated Ni-base ally, were virtually unaffected. The commercial cemented carbide sample, coated with TiN, showed a significantly better erosion resistance than the uncoated steels in the test.

[045] The screening test thus confirmed that structural components of a pump for liquid lead could be effectively protected from the bulk metal by stable coatings. Particular useful coatings comprise Al_2O_3 and ZrO_2.

[046] The screening test thus confirmed that structural components of a pump for liquid lead could be effectively protected from the bulk metal by stable coatings. Particular useful coatings comprise Al_2O_3 and ZrO_2. Pumps with such coatings or including components with such coatings are well suited for use in different systems for the generation of energy, such as but not limited to concentrated solar power and nuclear energy. They are particularly well suited for use in lead or LBE cooled reactors in the nuclear industry.

[047] The invention has mainly been described above with reference to a few embodiments. However, as is readily appreciated by a person skilled in the art, other embodiments than the ones disclosed above are equally possible within the scope of the invention, as defined by the appended patent claims.

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CLAIMS

1. A pump for pumping molten metal or molten salt, said pump comprising at least one component manufactured of a substrate and coated with one or more wear and erosion resistant surface layers,

wherein said substrate is provided with at least one intermediate binding layer and one outer layer, and said outer layer comprises at least one refractory oxide.

2. The pump according to claim 1, wherein the thickness of the surface coating is 0.2 µm to 1000 µm.

3. The pump according to claim 1, wherein the thickness of the surface coating is 5 – 600 µm.

4. The pump according to any one of the preceding claims, wherein the intermediate binding layer comprises at least one layer of TiN, preferably having a thickness of 0.1 – 5 µm.

5. The pump according to any one of the preceding claims, wherein the substrate is a cemented carbide and the refractory oxide outer layer comprises at least 90 % Al_2O_3.

6. The pump according to claim 5, wherein the outer layer comprises at least 99 % Al_2O_3.

7. The pump according to claim 5, wherein the cemented carbide comprises at least 80 % WC and a metallic binder, said metallic binder comprising at least one metal selected from the group of Co, Ni, Fe, Cr, Al, Mn, Mo, V, Ti, Ta, Zr and Nb.

8. The pump according to claim 7, wherein said metallic binder comprises Co and/or Fe and/or Ni and/or Cr and/or Mo in combination with Al.

9. The pump according to claim 8, wherein the binder is a Fe-Al, Ni-Al or a Ni-Cr-Mo-Al binder.

10. The pump according to any one claims 1 - 3, wherein

the substrate is a nickel based alloy comprising at least 30 wt. % Ni,

the outer layer comprises a refractory oxide based on ZrO_2, preferably yttria stabilized zirconia (YSZ), and the intermediate metallic binding layer comprises at least of one metal selected from the group Fe, Ni, Co, Cr or Al.

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