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HEAT TRANSFER SURFACE

The present invention relates to a heat transfer surface, to a heating element or condenser comprising said heat transfer surface, to a method of applying
5 said heat transfer surface and to a method for carrying out dropwise condensation employing said heat transfer surface.

During heating of a fluid via a heat transfer surface the surface will readily become coated with various deposits (eg. CaCO_3 , CaSO_4 and MgSO_4) which
10 are dissolved or partially dissolved in the fluid. Users of kettles in hard water areas will be well acquainted with this problem. Such deposits have an adverse effect on the heat transfer coefficient of the surface, which is reduced. This, in turn, leads to a decreased working efficiency of the heat transfer surface and/or a reduction in its service life.

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There is therefore a need for a heat transfer surface which alleviates the prior art problem of undesirable build-up of deposits.

Condensation processes employ the use of a condenser, also having a heat
20 transfer surface. Due to the nature of conventional metal materials used in the construction of heat exchangers, filmwise condensation occurs in industrial plants, for example in electric utility condensers and commercial distillation plant condensers [1]. Filmwise condensation results in a film of liquid forming over the heat transfer surface, the liquid typically being water which is a very
25 poor conductor of heat. This film then acts as an insulator and impedes efficient heat transfer across the heat transfer surface.

Dropwise condensation has received much attention in the past because of the inherent order of magnitude higher (eg. up to 20 times higher) steam-to-
30 condensing wall heat transfer coefficients that can be achieved compared with filmwise condensation.

To date, however, suitable dropwise condensation surfaces have not been



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developed to the satisfaction of condenser designers [2]. In this respect, it is a prerequisite for achieving dropwise condensation that the condensing surface possess a low surface energy [2]. Known metal surfaces possess a high surface energy with the result that steam condenses filmwise on such surfaces.

5 To obtain dropwise condensation on a metal surface, the surface energy must be reduced and the following methods have been tried [3]:

- (i) to apply organic promoters to a condenser surface;
- (ii) to coat the surface with organic polymer; and
- 10 (iii) to electroplate a layer of silver or gold on the surface.

Referring to (i), a solution of organic promoter (ie. non-wetting agent) may be wiped, brushed or sprayed onto the surface. However, such promoters wash off within a few hours of use, and dropwise condensation on the surface
15 changes to filmwise condensation [4]. In addition, the use of organic compounds often results in a deadly toxic coating, thereby limiting the application of such coatings.

Referring to (ii), many attempts have been made to produce long-term dropwise
20 surfaces by coating with organic polymers [5]. However, because the polymers such as PTFE (Teflon®) have a very low film conductivity, most of the benefits of dropwise condensation are offset by an increase in the thermal resistance of the polymer coating itself.

25 Referring to (iii), thin coatings of silver and gold have been shown to promote dropwise condensation. However, such coatings are impracticable from an economic point of view.

30 There is therefore a need for a heat transfer surface which may be used to achieve dropwise condensation.

The above prior art problems are alleviated by the present invention which,

according to a first aspect, provides a heat transfer surface comprising a layer of tetrahedral amorphous carbon and/or diamond-like carbon, and/or a composite thereof, wherein the carbon has an sp^3 bonding fraction of at least 70%.

- 5 Tetrahedral amorphous carbon (ta-C) is a substantially hydrogen-free form of diamond-like carbon with an sp^3 bonding fraction (ie. of the total carbon bonds present) that can be up to 90% or higher. The hydrogen content of ta-C is preferably less than 20% (w/w), and the sp^3 bonding fraction is typically at least 50%, preferably at least 60%, more preferably at least 70%. The
- 10 properties of ta-C are similar to those of crystalline carbon, with a short range tetrahedral order and a density approaching that of diamond. It has a similar hardness, chemical inertness and thermal stability to that of diamond. Large compressive stresses (up to 10 GPa) can be associated with the growth of high sp^3 fraction films, and these stresses can reduce the adhesion of such films at
- 15 higher film thicknesses. Improved adhesion is conveniently obtained by depositing an intermediate reactive metal or metal oxide layer to bond the film and the substrate together, allowing the deposition of ta-C onto any smooth surface material. Adhesion may also be promoted by depositing ta-C films using FCVA techniques on to a substrate which has been negatively biased
- 20 (typically between -500 to -5000V). Such biasing creates an interface surface which interacts well with the top surface layers of the substrate, thereby providing much improved adhesion. In addition, ta-C has important electrical properties. The band gap of ta-C is around 2eV (versus 5eV for crystalline diamond) making it a suitable candidate for use as a semi-conducting material
- 25 for a large area and for high temperature device applications.

Diamond-like carbon (DLC), unlike for example a-Si:H, has a nearly state-free optical gap without hydrogenation. It has a hydrogen content of typically 15-60% (w/w), and an sp^3 bonding fraction which is typically less than 50%.

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In preferred embodiments of the invention, the coating comprises or consists of ta-C. It is particularly preferred when temperatures in excess of 100°C are

likely to be encountered. Hydrogen atoms are very mobile and escape at elevated temperatures leading to a disruption in the structure of the carbon layer. With ta-C, the film is typically substantially hydrogen-free and any such structural disruption is minimised.

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The term "composite" means a combination (eg. an alloy) of ta-C or DLC with one or more additional components, typically metal components. The effect of the additional component is generally to modify a physical property of the selected carbon source, such as to increase the hardness and/or hydrophobicity of the coating.

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Examples of additional components include gold, silver, nickel, chromium, halides (preferably chloride or fluoride), Teflon® and Teflon®-like organic compounds. Where the additional component is a metal, that metal should preferably have a low surface energy. Where the additional component is Teflon® or Teflon®-like, films of greater thickness can be employed due to the lower stress in such composites. Such films generally have excellent toughness and adhesion properties, and improved thermal stability properties, compared with metal-containing composites.

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Composites are preferably employed when high temperatures (eg. 400°C and above) are encountered.

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According to a preferred embodiment the carbon-containing and/or composite layer has a maximum thickness of 1µm, more preferably a maximum thickness of 0.5µm. The thicker the layer is, the longer the service life will be. However, if the layer is excessively thick, the heat transfer coefficient may be compromised. For this reason, the carbon and/or composite layer is most preferably 0.06 to 0.1µm thick.

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The carbon and/or composite layer should be preferably clean and uniform in thickness. In this respect, a defect in the layer, especially at the surface, can

provide a high stress zone and/or a site for nucleation of scale. The macroparticle content of the coating is preferably zero or close thereto, whilst in practice it is difficult to avoid microparticle (less than $1\mu\text{m}$) deposits.

- 5 According to a preferred embodiment of the present invention, a heating element is provided having a heat transfer surface, said heat transfer surface comprising a layer of tetrahedral amorphous carbon and/or diamond-like carbon, and/or a composite thereof. Such a heating element has a prolonged service life and requires less frequent cleaning to remove deposits which may
10 otherwise cause a reduction in the heat coefficient of the element and an increase in the consumption of electricity.

In a specific embodiment of the invention described in more detail below, a heat transfer surface of the present invention is found to be less susceptible to
15 fouling (eg. by CaSO_4) than known surfaces. CaSO_4 is employed as the industry standard for assessing fouling resistance. In this respect, CaSO_4 (the major component of scale build-up in the Example) is more readily deposited and is much more difficult to break down than is CaCO_3 .

- 20 The heat transfer surface of the present invention may be employed in any apparatus in which heat transfer occurs and has particular application in *inter alia* water heaters such as kettles, dishwashers, washing machines and instant water heaters, and as an evaporator surface, for example in refrigerators and freezers.

25 Scale build-up at a heat transfer surface is often reduced when the fluid to be heated becomes "excited". For example, when a liquid is boiled, excited liquid molecules may strike the heat transfer surface and dislodge some of the scale. Conversely, when low fluid excitation levels occurs are experienced, little
30 physical removal of scale occurs. This is particularly so, for example, during pasteurisation of milk when it is highly undesirable for the milk to boil. During milk pasteurisation additional build-up is caused by milk proteins (eg. casein).

This may be problematic with conventional heat transfer surfaces. In use of embodiments of the heat transfer surface of the present invention such deposits have been advantageously reduced by approximately 50%.

- 5 According to another preferred embodiment, there is provided a condenser for use in dropwise condensation, said condenser having a heat transfer surface comprising a layer of tetrahedral amorphous carbon and/or diamond-like carbon, and/or a composite thereof. Use of the heat transfer surface in such a condenser permits a reduced condenser pressure to be employed during
10 condensation which, in turn, results in an improved plant efficiency. Alternatively, use of the claimed heat transfer surface permits a reduced size condenser to be employed.

It is estimated that a 10 mbar decrease in condenser pressure results in 0.9%
15 turbine work increase in a 600 MW coal fired plant, 1.2% in a 900 MW nuclear plant and 0.4% in a combined cycle plant. In the case of a 600 MW plant, the corresponding reduction in coal consumption would be 1,000 tonnes per year, with corresponding reductions in pollution. The introduction of dropwise condensation in power production processes constitutes energy savings.

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A heat transfer surface of the present invention may also be used in a new type of shell-and-tube dropwise condenser, for which overall heat transfer coefficients are doubled compared with current filmwise condensers. Hence, the heat transfer area may be reduced by half and considerable materials and
25 energy may be saved. For example, the cost of producing electricity in a power plant may be reduced by a reduction in the number of tubes required or by a reduction of the pressure in the turbine condenser. In typical UK conditions, a 5 mbar pressure reduction is possible, which corresponds to an increase in turbine work of 0.5% in a 600 MW coal fired plant. In turn, this
30 would result in a saving of 9,000 tonnes per year of coal and consequently 30,000 tonnes per year of CO₂ emissions [1].

In the case of a condenser, surfaces on both sides of, say, a condenser plate, may comprise a heat transfer surface coated according to the present invention. Such a condenser would benefit from both dropwise condensation on one side and from reduced fouling on the other where, for example, the
5 coolant is water, particularly sea water.

According to a second aspect of the present invention, there is provided a method for preparing a heat transfer surface, comprising applying a layer of tetrahedral amorphous carbon and/or diamond-like carbon, and/or a composite
10 thereof, to the surface.

The surface to be coated with the layer of the present invention is preferably smooth. This may be achieved, for example, by cleaning and/or polishing. Should the surface be greasy, an organic detergent may be employed.
15 Following initial cleaning, the surface may then be subjected to ultrasonic cleaning in a water bath, optionally containing further detergent. The cleaned surface may be then washed with deionised water.

Stainless steel metal is the industry standard heat transfer surface and provides
20 an ideal surface to be coated with a layer according to the present invention. Alternative surfaces include copper and aluminium, though the invention is of application generally to all such surfaces.

Various techniques may be used to deposit a carbon and/or a composite film
25 in accordance with the present invention, see for example the *Handbook of Deposition Technologies for Films and Coatings* (1994), Science and Technology and Applications, second edition (ed. Rointan F. Bunshah), NOYES PUBLICATIONS, Park Ridge, New Jersey, USA.

30 A film may be deposited on any surface capable of conducting electricity. The carbon film may be applied by Plasma Enhanced Chemical Vapour Deposition (PECVD). Examples of this technique are "RF Parallel Plate Plasma Deposition"

and "Hot Wire Deposition". A general feature of the most common techniques is that the transport of the active particles towards a substrate is determined by diffusion.

5 Alternatively, plasma deposition techniques may be employed based on the expansion of a thermal plasma into a vessel at low pressure. In this technique, the transport of particles towards the substrate is determined by direct transport.

10 In particular, a cathodic arc apparatus may be employed for applying the carbon and/or composite layer as disclosed for example in US 5,279,723. US 5,279,723 employs a cathodic arc ion source apparatus in which there is no line-of-site from the arc spot on the target to the substrate which is to be coated, and the present invention may employ this or similar apparatuses.
15 Alternatively, apparatuses having a line-of-site may be employed. This is because a homogenous, macroparticle-free layer of carbon is not critical for the purpose of the present invention. Other suitable methods are disclosed by the present applicants in WO 96/26531, WO 96/26532, WO 98/03988, PCT/IB98/01764, PCT/IB98/01765, PCT/IB98/01762 and PCT/IB98/01768.

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Referring to the above methods employing a plasma source, a O₂ or N₂-containing plasma is a further option. Such gases help to increase the surface energy of the surface to be coated. This, in turn, leads to improved adhesion of the film to the surface.

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The present invention is now described by reference to the following example in which:-

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Figure 1 illustrates the results of Example 1, wherein the DLC and ta-C sputtered surfaces are in accordance with the present invention. The H-implanted surface and bare surface represent conventional heat transfer surfaces.

Figure 2 illustrates the heat transfer properties of various coated surfaces. The TiNF surface is applied by CVD and employs a metal organic promoter. The use of an organic promoter, as illustrated, frequently results in a deadly toxic coating. In addition, the TiNF coating is less durable than a ta-C based coating and the coating costs are much higher.

Example 1 - CaSO_4 fouling test results during pool boiling

Heat rod: sputtered with tetrahedral amorphous carbon (ta-C), by Nanyang Technological University.

Test condition: CaSO_4 Solution: 1.6 g/l, Heat Flux: 100 kW/m².

Results: see Figures 1 and 2.

For a bare heater rod (No.432), the average final heat transfer coefficient was about 1900 W/m².K. After the heater rod (No.432) was coated with ta-C, the average final heat transfer coefficient (after approximately 60 hours) was increased to about 5000 W/m².K, as show in the following chart. It was observed that many tiny white flakes were dancing in the solution. These flakes were scale deposits which had broken off the heat transfer surface. During the entire test, only a few parts of the heat transfer surface were covered with a very thin layer of deposit, and most of the heat transfer surface was deposit-free.

Previous fouling test results of a H-implanted heater rod and a DLC sputtered heater rod are also shown in Figure 1 for comparison. By comparing the final heat transfer coefficients (see Figure 1), the ta-C coated surface provided the best results 5000 W/m².K after approximately 60 hours, followed by the DLC coated surface 4000 W/m².K after approximately 60 hours.

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Table 1 - Final Heat Transfer Coefficients for Different Treated Surfaces

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Heating Element: Coating	Final Heat Transfer Coefficient [W/m ² .K]	Increase [%]
None	1900	-
H (implanted)	3800	100
DLC	4000	110
ta-C	5000	163

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References

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- [2] Tanasawa, I., "*Dropwise condensation - The way to practical applications.*" Proc. 6th Int. Heat Transfer Conf., vol.6, 393 (1978)
- [3] Tanasawa, I., "*Advances in Condensation Heat Transfer*". Advances in Heat Transfer, vol. 21, 55 (1991)
- [4] Blackman, L.C.F., Dewarm, M.J.S. and Hampson, H., "*An investigation of compounds promoting the dropwise condensation of steam*" J. Appl. Chem. vol.7, 160 (1957)
- [5] Marto, P.J., Looney, D.J., Rose, J.W. and Wanniarachchi, A.S., "*Evaluation of organic coatings for the promotion of dropwise condensation of steam*", Int. J. Heat Mass Transfer, vol.29, No.8, 1109 (1986)

Claims:

1. A heat transfer surface, comprising a layer of tetrahedral amorphous carbon and/or diamond-like carbon, and/or a composite thereof, wherein the carbon has an sp³ bonding fraction of at least 70%.
2. A surface as claimed in Claim 1, comprising tetrahedral amorphous carbon.
3. A surface as claimed in Claim 2, wherein the carbon has an sp³ bonding fraction of at least 80%.
4. A surface as claimed in any preceding claim, wherein the carbon is in the form of a composite.
5. A surface as claimed in any preceding claim, wherein the layer has a maximum thickness of 1 μ m.
6. A heating element for heating a fluid, said heating element having a heat transfer surface as claimed in any preceding claim.
7. A heating element as claimed in Claim 6, wherein each exposed surface of said heating element is substantially coated with a layer of carbon and/or composite as defined in any of Claims 1-5.
8. A heating element as claimed in Claim 6 or 7, wherein the fluid is a liquid.
9. A heating element as claimed in Claim 8, wherein the liquid is an aqueous solution.
10. A water heater comprising a heat transfer surface as claimed in any of Claims 1-5 and/or a heating element as claimed in any of Claims 6-9.
11. A water heater as claimed in Claim 10, wherein said water heater is a kettle, a dish washer, a washing machine, or an instant water heater.

12. A condenser for use in dropwise condensation, said condenser comprising a heat transfer surface as claimed in any of Claims 1-5.
13. A turbine comprising a condenser as claimed in Claim 12.
14. A method for preparing a heat transfer surface as claimed in any of Claims 1-5, comprising applying a layer of tetrahedral amorphous carbon and/or diamond-like carbon, and/or a composite thereof, to a surface.
15. A method as claimed in Claim 14, wherein the layer is applied by a cathode arc source.
16. A method for carrying out dropwise condensation, wherein a condenser is employed having a heat transfer surface as claimed in any of Claims 1-5.
17. Use of tetrahedral amorphous carbon and/or diamond-like carbon, and/or a composite thereof, as a heat transfer surface.
18. A heat transfer surface substantially as hereinbefore described with reference to the examples.