Title: COATING WITH HARD WEAR AND NON-STICK CHARACTERISTICS

Abstract: The invention relates to a coating, an article with a coating and method of applying the coating which has improved non stick characteristics. The coating includes or is wholly formed with a metal nitride which is preferably deposited using a closed field unbalanced magnetron ion sputter plating process and is found to provide a coating which is especially useful in mould tools to prevent plastics material being formed in the mould from sticking to the surface of the mould tool.
Coating with Hard Wear and Non-stick Characteristics.

The invention to which this application relates is to the provision of a coating which has non-stick or reduced adherence characteristics. A further aim is to provide improvements to articles or tools which have a surface to which said coating can be applied to improve the operation or use of the same.

In particular, but not necessarily exclusively, the invention relates to the forming of polymer materials in said forming tools and to the method and apparatus for application of the coating.

When forming polymers, namely plastics, rubbers and thermosets, the material, when in a fluid state, is introduced into one or a series of moulds which control the shape to be taken by the material. Once the material hardens, typically by cooling or curing, the moulds can be removed and/or the product is ejected from the moulds, typically by ejector pins, to leave the formed product. However, a problem which is commonly experienced is that when removing the forming tool parts, or the product, portions of the material remains attached to the forming tool. This causes damage to the product, possible rejection of the product for quality reasons and can also cause damage to the relatively expensive tool parts. It also requires, if the tool mould is to be re-used, that the tool is cleaned between forming operations. This is inconvenient and reduces productivity. While it is known to be able to use mould release agents, for certain products, such as CD's and optical components, these release agents cannot be used due to the need to keep the products particularly clean.

Generally, in order to attempt to reduce the sticking of the polymer material, the forming tool surfaces need to be as smooth as possible, but even with well polished tools,
significant adhesion of the material to the surfaces of the same still takes place.

While the problem is described with respect to the moulding tools for use on forming plastics material it should be appreciated that these problems occur in many different instances and as a result the advantages which are hereby described can be applied to many different uses.

The aim of the present invention is to provide a means of improving the use of articles where adhesion of material can be problematic, one such use being with forming tools. The aim is to provide means such that the condition of those surfaces where lack of adhesion is advantageous can be improved by applying a coating onto the same. A further aim of the invention is to provide a coating material which achieves the desired reduction in material adhesion and to define suitable apparatus and method for applying the coating.

In a first aspect of the invention there is provided an article with at least one surface conditioned to have a reduced tendency for other materials to adhere to the same and wherein the surface is conditioned by the application of a coating thereto, said coating layer including a metal nitride.

Typically the article exhibits a reduced tendency for other materials to adhere to the same and the coating layer includes the metal nitride and has a hexagonal structure.

In one embodiment the coating layer comprises a metal nitride. In an alternative embodiment the coating includes the metal nitride but also includes other materials, said materials applied to provide certain desired characteristics for the coating.
In one embodiment the coating layer includes any or any combination of Cr2N, CrN, Ni3N, NiCr(N).

Preferably the metal nitride includes nickel and in a preferred embodiment the material is Nickel Chromium Nitride (NiCr(N)).

In one embodiment the surfaces to be coated are provided to come into contact with a polymer material and to resist or reduce adhesion therewith and in one embodiment at least those surfaces of the article which are to contact with the polymer material are provided with the coating to reduce the tendency of the polymer material to stick to the same.

In whichever embodiment, the coating material is applied to form the coating in an oriented manner, typically a highly oriented manner, in which more than 50% of the basal planes of the hexagonal structure lie substantially parallel with the surface to which the coating is applied.

In one embodiment, the metal used in the metal nitride is a non-ferromagnetic attractive metal.

In one embodiment the article on which the surfaces are coated is a forming tool for use in a moulding process, said forming tool having a coating layer applied to those surfaces which contact with the material to be formed in the tool. In one embodiment the forming tool is for use in the formation of polymer material into an item of a shape defined by the external surfaces of the coating applied to the forming tool.

In a further aspect of the invention there is provided a coating applied to a surface of an article to form an external surface thereof, said coating including an outer surface of a metal
nitride, said metal nitride having a hexagonal structure with a highly oriented basal plane arrangement.

In one embodiment the metal nitride has a highly oriented configuration in that the majority of the basal planes are substantially parallel with the surface to which the material is applied. Preferably the whole coating is so oriented.

In one embodiment the material used to form at least the outer surface of the coating is Nickel Chromium nitride.

In a further aspect of the invention, there is provided a coating applied using Closed Field Unbalanced Magnetron Sputter Ion Plating apparatus and the coating has at least one layer which is of a hexagonal structure with high orientation of the basal planes to lie parallel with the surface of the article to which the coating is applied.

In one embodiment the coating is multi layered and at least the outer layer of the coating has the hexagonal structure and the high orientation of the basal planes.

In one embodiment the at least outer layer includes or comprises Cr2N.

In one embodiment the sputtering method produces smooth external surface with a dense form and with a minimum of defects. Typically the Closed Field arrangement of Unbalanced magnetrons in the apparatus gives very high ion current densities during the coating process hence producing the very dense coatings.

In a further aspect of the invention there is provided a method for the application of a coating of the type herein described and
including a metal nitride said method comprising the steps of sputtering Nickel in a nitrogen atmosphere to produce an Ni3N structure on the surface to be coated.

Preferably the method includes the sputtering of material from a NiCr target in a nitrogen atmosphere.

Typically, any of the coatings, Cr2N, Ni3N, NiCr(N), deposited using CFUBMSIP in accordance with the invention, are smooth and have dense structures, are hard and have a hexagonal structure.

Typically by applying the metal nitride material using the CFUBMSIP apparatus, a coating is achieved which has high orientation and has basal planes which are parallel to the surface to which the coating is applied.

A specific embodiment of the invention is now described in which the coating is applied using apparatus as shown in Figure 1 and which is apparatus referred to as a closed field unbalanced magnetron sputter ion plating apparatus which is subject to protection in the applicant's patent GB2258343 and reference is hereby made to the contents of that patent.

In Figure 1 there is illustrated apparatus in plan and in a schematic manner in a form which can be used for a batch coating process but in-line processes are equally applicable. In this apparatus there is provided a coating chamber 2 in which there is disposed two sets of opposing unbalanced magnetrons 4,6; 8,10. Each of the unbalanced magnetrons include a target 12 of suitable material to allow the coating to be formed. The magnetrons are arranged to operate in a closed field configuration in that the magnetrons are arranged around a carrier 9 in the chamber 2 which is centrally spaced relative to
the magnetrons. The magnetrons are arranged so that adjacent magnetrons have outer magnetic assemblies 14 of opposite polarity, to those adjacent thereto hence allowing magnetic field lines to link adjacent magnetrons so as to produce a substantially closed ring of magnetic flux which substantially traps all electrons generated in the system and increases the level of ionisation surrounding the carrier. It should be appreciated that some of the unbalanced magnetrons may be replaced by arrays of magnets with suitable magnetic configuration to retain the closed filed of magnetic flux in the coating chamber.

The carrier 9 is provided in the form of a drum driven to rotate about axis 13 and on the external surface 11 of which can be mounted the devices or items to be coated. The devices are mounted such that the surface of the same which is to be coated, faces towards the unbalanced magnetrons.

Inlet means are provided to allow the selective introduction of working gases into the chamber and pumps are provided in order to allow the pressure in the chamber to be controlled.

In operation, power is applied to the magnetrons under controlled conditions via power supplies 20, 21, 22, 23 rotating carrier receive coating flux material from the targets as they pass the same and as a result the layer of the material is built up to the required thickness of coating. The carrier is insulated from the body of the machine to allow it to float electrically (or for a bias voltage to be applied).

In this specific use at least one, but typically two Cr targets are utilised 12' and an NiCr material target or targets 12" is/are utilised in the closed field arrangement. By the selective operation of the deposition means a multilayer coating is applied.
to the surface or surfaces of the item to be coated and which item is positioned within the coating apparatus to be exposed to the deposited material. A suitable gas to be introduced into the coating chamber in this case would be Nitrogen. In this example a coating structure of Cr2N/NiCr(N)Cr2N/NiCr(N) is deposited and has a highly oriented hexagonal structure. This is achieved by the sequential operation of the deposition means to cause the sputtering of material from either set of targets 12' or 12" to form the inner and outer layers respectively and co-sputtering of targets 12', 12" of required to form the middle layer.

Thus in accordance with the invention there is provided a Cr2N containing coating which is applicable to all surfaces and in particular to the surfaces of forming tools which are to be used to form polymer materials and to prevent or reduce the adhesion of the polymer to the surface of said tools.

In an alternative embodiment a Ni3N coating can be applied or yet further a NiCr(N) coating.

As described above by the selective operation of the coating apparatus coatings comprising a series of layers can be applied to form the coating, such as those comprising Cr2N and Ni3N layers or Cr2N and NiCr(N) layers, or multilayer coatings comprising Ni3N and NiCr(N) layers.

It should therefore be appreciated that in accordance with the invention, any hard metal nitride, carbo nitride, oxide, or oxynitride with an oriented basal plane and hexagonal structure can be utilised to advantage in accordance with the invention.

Specific examples of the invention are now described in a non limiting manner.
The coating in the form of NiCr(N) in the following examples was produced using closed-field unbalanced magnetron sputter ion plating.

Example 1:
Adhesion of a grade of low-density polyethylene (LDPE) and a grade of high-density polyethylene (HDPE) were investigated against an NiCr(N) coating in accordance with the invention. The contact angle of LDPE in a molten state was 50° compared with 44° in the case of uncoated stainless steel, showing a lower tendency for the polymer to spread on NiCr(N). The contact angle of HDPE was 72° against NiCr(N) and 60° against uncoated stainless steel.

Example 2:
An adhesion test method was used to evaluate the adhesion of polymers to NiCr(N) coatings. The method involved the compression moulding of polymer onto an uncoated and a coated stainless steel sheet, and subsequent measurement of the stress required for the separation of the polymer from the coated sheet and the uncoated sheet. The stress required to separate LDPE in the case of an uncoated stainless steel sheet was >0.46 MPa while no stress was experienced in the case of NiCr(N) coated sample.

Example 3:
An adhesion test method similar to that described in example 2 was carried out to evaluate the adhesion of an epoxy resin cured onto as NiCr(N)-coated steel sheet. While a significant amount of stress was required to separate the cured resin from an uncoated steel sample, the polymer was separated from the NiCr(N)-coated sample without any need for additional stress.
Typically the multi layered coating tends to have a harder composition and is denser than a single layer coatings. As the material which comes into contact with the coating when the same is used in a forming tool, can be abrasive and the combination of hard wear resistance properties and non-stick properties which can be achieved in accordance with this invention is an important advantage.

While the non-stick properties of the coatings are of significant advantage it is also important that the same are hard and wear resistant. Metal nitrides are hard and wear resistant and therefore with metal nitride containing coatings in accordance with the invention there is the required combination of non-stick and wear resistance. Thus while CrN is smooth, hard and wear resistant it does not have the non stick properties because it is of a cubic form. Coatings with Cr2N are smooth, hard and wear resistant and are also non-stick because of the hexagonal structure.
Claims

1. An article with at least one surface conditioned to have a reduced tendency for other materials to adhere to the same and wherein the surface is conditioned by the application of a coating thereto, said coating layer including a metal nitride.

2. A coating according to claim 1 wherein the coating has a hexagonal structure

3. An article according to claim 1 wherein the coating layer wholly comprises a metal nitride.

4. An article according to claim 1 wherein the coating includes metal nitride and further materials.

5. An article according to claim 1 wherein the coating layer includes any or any combination of Cr2N, CrN, Ni3N, NiCr(N).

6. An article according to claim 1 wherein the metal nitride includes nickel.

7. An article according to claim 5 wherein the layer includes nickel chromium nitride.

8. An article according to claim 1 wherein the surface which is coated is provided to come into contact with a polymer material and to resist or reduce adhesion therewith.

9. An article according to claim 8 wherein at least those surfaces of the article which are to contact with the polymer material are provided with a coating.
10. An article according to claim 1 wherein the coating material is applied to form a coating in an oriented manner.

11. An article according to claim 10 wherein the coating material is applied to form a coating in a highly oriented manner in which more than 50% of the basal planes of the hexagonal structure lie substantially parallel with the surface to which the coating is applied.

12. An article according to claim 1 wherein the metal used in the metal nitride is a non-ferromagnetic attractive metal.

13. An article according to claim 1 wherein the article is a forming tool for use in a moulding process.

14. An article according to claim 13 wherein the coating layer is applied to those surfaces of the article which contact with the material to be formed in the tool with the polymer material formed into an item of a shape defined by the external surfaces of the coating applied to the forming tool.

15. A coating applied to a surface of an article to form an external surface thereof, said coating including at least an outer surface of a metal nitride, said metal nitride having a hexagonal structure with a highly oriented basal plane arrangement.

16. A coating according to claim 15 wherein the metal nitride has a highly oriented configuration in that the majority of the basal planes are substantially parallel with the surface to which the material is applied.

17. A coating according to claim 16 wherein the entire coating is so oriented.
18. A coating according to claim 15 wherein the material used to form at least the outer surface of the coating is nickel chromium nitride.

19. A coating applied using closed field unbalanced magnetron sputter ion plating apparatus, said coating having at least one layer which is of a hexagonal structure with high orientation of the basal planes to lie parallel with the surface of the article to which the coating is applied.

20. A coating according to claim 19 wherein the coating is multilayered and at least the outer layer of the coating has the hexagonal structure and the high orientation of the basal planes.

21. A coating according to claim 19 wherein at least the outer layer includes or comprises Cr2N.

22. A method for the application of a coating of the type herein described and including a metal nitride, said method comprising the steps of sputtering nickel in a nitrogen atmosphere to produce an Ni3N structure on the surface to be coated.

23. A method according to claim 22 wherein the method includes sputtering material from a NiCR target in a nitrogen atmosphere.

24. A method according to claim 23 wherein the sputter deposition takes place in a closed field unbalanced magnetron sputter ion plating apparatus.

25. A method according to claim 22 wherein the coating which is applied is smooth, has a dense structure, is hard and has a hexagonal structure.