

TITLE OF THE INVENTION

SURFACE MODIFYING PROCESS FOR METAL PRODUCTS

BACKGROUND OF THE INVENTION

The present invention relates to a surface
5 modifying process for metal products such as dies for
producing glass articles by press work, dies for pre-
paring metal products by forging or press work and molds
for producing plastic articles by injection molding.

Dies are used for press work for producing glass
10 articles such as plates for optical glass disks for use
as optical disk memories in computers, video and audio
devices, etc., plates for glass hard disks for use in
computers, glass lenses for use as optical elements,
front glass panels of cathode-ray tubes for TV receiv-
15 ers, computer displays, etc., and glass panels for use
in liquid-crystal displays. Dies of stainless steel,
cemented carbide, etc. are already known which are
coated over the forming surface thereof with a platinum
film in order to give improved releasability and oxida-
20 tion resistance to the die. Dies for preparing metal
products by forging or press work and molds for produc-
ing plastic articles by injection molding are also known
which are coated with a platinum film to improve the

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releasability and oxidation resistance of the forming surface thereof.

However, the conventional press dies, for example, for glass products have the problem that the platinum
5 film peels off or the forming surface wears within a relatively short period of time when used for continuous press work, i.e., when used for about 10000 to about 20000 shots, hence a short life. Accordingly the die needs to be replaced in its entirety after a relatively
10 small number of cycles to result in the problem of an increased cost.

DISCLOSURE OF THE INVENTION

An object of the present invention is to overcome the above problems and provide a surface modifying
15 process for metal products which is capable of improving the peel resistance of a platinum film formed on the surface of the metal product and giving improved wear resistance to the surface.

The present invention provides a first process for
20 modifying a surface of a metal product which process is characterized by injecting platinum ions into the surface of the metal product by ion implantation, thereafter forming a platinum film on the surface and further injecting platinum ions into the resulting

surface by ion implantation.

According to the first process, the platinum ions implanted first, the platinum ions in the platinum film and a platinum ion that is injected afterwards are
5 assimilatory combined, resulting in an improvement of both the adhesion of the platinum film to the metal product, and of the exfoliation resistance of the platinum film. This affords a prolonged life to the metal product and renders the product usable for
10 increased cycles before replacement to result in a lower cost. Moreover the platinum film retains oxidation resistance without impairment. Especially in the case where the metal product is a press die for glass products, forging or press die for metal products or
15 mold for preparing plastic products by injection molding, the process will not impair the releasability of the product from the die or mold used.

The present invention provides a second process for modifying a surface of a metal product which process is
20 characterized by injecting nitrogen ions and platinum ions into the surface of the metal product in this order by ion implantation, thereafter forming a platinum film on the surface and further injecting platinum ions into the resulting surface by ion implantation.

The second process uses nitrogen ions for ion implantation, thereby giving the base metal of the metal product enhanced strength and improving the wear resistance of the product. The platinum ions implanted first, the platinum ions in the platinum film and a platinum ion that is injected afterwards are assimilatory combined, resulting in an improvement of both the adhesion of the platinum film to the metal product, and of the exfoliation resistance of the platinum film.

10 This affords a prolonged life to the metal product and renders the product usable for increased cycles before replacement to result in a lower cost. Moreover the platinum film retains oxidation resistance without impairment. Especially in the case where the metal

15 product is a press die for glass products, forging or press die for metal products or mold for preparing plastic products by injection molding, the process will not impair the releasability of the product from the die or mold used.

20 The present invention provides a third process for modifying a surface of a metal product which process is characterized by injecting nitrogen ions, carbon ions and platinum ions into the surface of the metal product in this order by ion implantation, thereafter forming a

platinum film on the surface and further injecting platinum ions into the resulting surface by ion implantation.

The third process uses nitrogen ions and carbon ions for ion implantation, thereby giving the base metal of the metal product enhanced strength and improving the wear resistance of the product. The platinum ions implanted first, the platinum ions in the platinum film and a platinum ion that is injected afterwards are assimilatory combined, resulting in an improvement of both the adhesion of the platinum film to the metal product, and of the exfoliation resistance of the platinum film. This affords a prolonged life to the metal product and renders the product usable for increased cycles before replacement to result in a lower cost. Especially in the case where the metal product is a press die for glass products, forging or press die for metal products or mold for preparing plastic products by injection molding, the carbon ions implanted improve the releasability of the product from the die or mold used. Moreover the implantation of ions will not impair the oxidation resistance of the platinum film.

The metal product to be modified over the surface by these three processes of the invention is, for

example, a die for preparing glass products by press work. However, the three processes of the invention are usable for the surface modification not only of dies of this type but also of dies for preparing metal products by forging or press work, molds for producing plastic articles by injection molding, and metal products such as tools.

The metal product to be surface-modified is made, for example, from stainless steel, cemented carbide, or tool steel alloy for hot working dies.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The surfaces of metal products are modified by the first process which comprises injecting platinum ions into the surface of the metal product by ion implantation, thereafter forming a platinum film on the surface and further injecting platinum ions into the resulting surface by ion implantation. In this first process, the platinum ion implantation before and after forming the platinum film is effected preferably in an amount of $1 \text{ to } 5 \times 10^{15} \text{ ions/cm}^2$ at an acceleration voltage of 10 to 200 kev and ionic current of 10 to 100 mA. These ranges of conditions have been determined by various experiments. The platinum film to be formed by the first process preferably has a thickness of 0.1 to

0.5 μm . If the film is less than 0.1 μm , it is difficult to form a platinum film evenly and if the thickness exceeds 0.5 μm , the volume of a platinum ion to be injected after the formation of platinum film has to be increased, resulting in the risk that the surface of the metal product chaps.

The surface of the metal product is modified alternatively by the second process which comprises injecting nitrogen ions and platinum ions into the surface of the metal product in this order by ion implantation, thereafter forming a platinum film on the surface and further injecting platinum ions into the resulting surface by ion implantation. In the second process, it is desirable to effect the nitrogen ion implantation in an amount of 1 to 5×10^{15} ions/cm² at an acceleration voltage of 10 to 100 keV and ionic current of 10 to 100 mA. These ranges of conditions have been determined by various experiments. The platinum ion implantation before and after forming the platinum film is effected preferably in an amount of 1 to 5×10^{17} ions/cm² at an acceleration voltage of 10 to 200 keV and ionic current of 10 to 100 mA. These ranges of conditions have been determined by various experiments. It is desired that the platinum film to be formed in the

second process be 0.1 to 0.5 μm in thickness for the same reasons described for the first process.

Further alternatively, the surface of the metal product is modified by the third process which comprises
5 injecting nitrogen ions, carbon ions and platinum ions into the surface of the metal product in this order by ion implantation, thereafter forming a platinum film on the surface and further injecting platinum ions into the resulting surface by ion implantation. In the third
10 process, it is desirable to effect the nitrogen ion implantation in an amount of 1 to 5×10^{15} ions/ cm^2 at an acceleration voltage of 10 to 100 kev and ionic current of 10 to 100 mA. These ranges of conditions have been determined by various experiments. Preferably the
15 carbon ion implantation is effected in an amount of 1 to 3×10^{17} ions/ cm^2 at an acceleration voltage of 10 to 100 kev and ionic current of 10 to 100 mA. These ranges of conditions have been determined by various experiments. The platinum ion implantation before and after forming
20 the platinum film is effected preferably in an amount of 1 to 5×10^{17} ions/ cm^2 at an acceleration voltage of 10 to 200 kev and ionic current of 10 to 100 mA. These ranges of conditions have been determined also by various experiments. It is desired that the platinum film to be

formed in the third process be 0.1 to 0.5 μm in thickness for the same reasons described for the first process.

In the third process, it is desirable to inject
5 palladium ions into the surface of the metal product by ion implantation after the nitrogen ion implantation and before the carbon ion implantation. The palladium ion implantation is effected in an amount of 1 to 5×10^{15} ions/ cm^2 at an acceleration voltage of 10 to 200 keV and
10 ionic current of 10 to 50 mA. These ranges of conditions have been determined by various experiments.

EXAMPLES

Example 1.

Platinum ions were injected by ion implantation in
15 an amount of 1×10^{15} ions/ cm^2 at an acceleration voltage of 100 keV and ionic current of 50 mA into the forming surface of a die made of JIS SUS306 for preparing plates for glass hard disks by press work. The forming surface of the die was then coated with a platinum film having a
20 thickness of 0.1 μm by sputtering. Platinum ions were thereafter injected by ion implantation in an amount of 1×10^{15} ions/ cm^2 at an acceleration voltage of 100 keV and ionic current of 50 mA into the resulting forming surface of the die. In this way, a modified surface was

formed on the die.

To evaluate the die thus obtained, the die was used for pressing blank plates of alkali zinc borosilicate base glass substrate (86 mm in diameter and 1.2 mm in thickness) at a die temperature of 555 to 560° C under a pressure of 48.5 t to prepare plates for glass hard disks having a diameter of 88 to 90 mm and a thickness of 0.8 mm. When this press work was continuously conducted, the platinum film was found free of peeling until 133900 shots were made. No wear was found in the die forming surface after the continuous press work of 133900 shots.

Example 2

Nitrogen ions were injected by ion implantation in an amount of 1×10^{15} ions/cm² at an acceleration voltage of 100 kev and ionic current of 50 mA into the forming surface of a die made of JIS SUS306 for preparing plates for glass hard disks by press work. Platinum ions were then injected by ion implantation in an amount of 1×10^{17} ions/cm² at an acceleration voltage of 100 kev and ionic current of 50 mA into the forming surface of a die. Subsequently, the forming surface of the die was coated with a platinum film having a thickness of 0.1 μ m by sputtering. Platinum ions were injected by ion

implantation in an amount of 1×10^{17} ions/cm² at an acceleration voltage of 100 kev and ionic current of 50 mA into the resulting forming surface of the die. In this way, a modified surface was formed on the die.

5 The die thus obtained was used for continuous press work to prepare plates for glass hard disks under the same conditions as in Example 1 except that the die temperature was 590 to 595° C. Consequently, the platinum film was found free of peeling until 930000
10 shots were made. Wear of about 0.008 to about 0.01 mm was found in the die forming surface after the continuous press work of 930000 shots.

Example 3

Nitrogen ions were injected by ion implantation in
15 an amount of 5×10^{15} ions/cm² at an acceleration voltage of 100 kev and ionic current of 50 mA into the forming surface of a die made of JIS SUS306 for preparing plates for glass hard disks by press work. Carbon ions were then injected by ion implantation in an amount of $1 \times$
20 10^{17} ions/cm² at an acceleration voltage of 100 kev and ionic current of 50 mA into the forming surface of the die. Subsequently, platinum ions were injected by ion implantation in an amount of 2×10^{17} ions/cm² at an acceleration voltage of 100 kev and ionic current of 50

mA into the forming surface of a die. The forming surface of the die was thereafter coated with a platinum film having a thickness of 0.1 μm by sputtering.

Platinum ions were injected by ion implantation in an amount of 1×10^{17} ions/cm² at an acceleration voltage of 100 keV and ionic current of 50 mA into the resulting forming surface of the die. In this way, a modified surface was formed on the die.

The die thus obtained was used for continuous press work to prepare plates for glass hard disks under the same conditions as in Example 1 except that the die temperature was 590 to 600° C. Consequently, the platinum film was found free of peeling until 1410000 shots were made. Wear of about 0.01 to about 0.05 mm was found in the central portion of the die forming surface, and wear of about 0.008 to about 0.01 mm in the peripheral portion thereof after the continuous press work of 1410000 shots.

Example 4

Nitrogen ions were injected by ion implantation in an amount of 5×10^{15} ions/cm² at an acceleration voltage of 100 keV and ionic current of 50 mA into the forming surface of a die made of WC-Co cemented carbide (JIS K20) for preparing plates for glass hard disks by press

work. Palladium ions were then injected by ion implantation in an amount of 1×10^{15} ions/cm² at an acceleration voltage of 100 kev and ionic current of 50 mA into the forming surface of the die. Carbon ions
5 were further injected by ion implantation in an amount of 1×10^{17} ions/cm² at an acceleration voltage of 100 kev and ionic current of 50 mA into the forming surface of the die. Subsequently, platinum ions were injected by ion implantation in an amount of 2×10^{17} ions/cm² at an
10 acceleration voltage of 100 kev and ionic current of 50 mA into the forming surface of a die. The forming surface of the die was thereafter coated with a platinum film having a thickness of 0.1 μ m. Platinum ions were injected by ion implantation in an amount of 1×10^{17}
15 ions/cm² at an acceleration voltage of 100 kev and ionic current of 50 mA into the resulting forming surface of the die. In this way, a modified surface was formed on the die.

The die thus obtained was used for continuous press
20 work to prepare plates for glass hard disks under the same conditions as in Example 1 except that the die temperature was 670 to 680° C. Consequently, the platinum film was found free of peeling until 1210000 shots were made. Wear of about 0.008 to about 0.01 mm

was found in the die forming surface after the continuous press work of 1210000 shots.

Comparative Example

A platinum film having a thickness of 0.5 μm was
5 formed by sputtering on the forming surface of a die
made of JIS SUS306 for preparing plates for glass hard
disks by press work.

The die thus obtained was used for continuous press
work to prepare plates for glass hard disks under the
10 same conditions as in Example 1 except that the die
temperature was 590 to 600° C. Consequently, the
platinum film was found to have been peeled after 10000
shots were made. Wear of about 0.05 to about 0.08 mm
was found in the die forming surface after the
15 continuous press work of 10000 shots.

What is claimed is:

1. A process for modifying a surface of a metal product which process is characterized by injecting platinum ions into the surface of the metal product by ion implantation, thereafter forming a platinum film on the surface and further injecting platinum ions into the resulting surface by ion implantation.

2. A surface modifying process for a metal product according to claim 1 wherein the platinum ion implantation before and after forming the platinum film is effected in an amount of $1 \text{ to } 5 \times 10^{15} \text{ ions/cm}^2$ at an acceleration voltage of 10 to 200 kev and ionic current of 10 to 100 mA.

3. A surface modifying process for a metal product according to claim 1 or 2 wherein the platinum film to be formed has a thickness of 0.1 to 0.5 μm .

4. A process for modifying a surface of a metal product which process is characterized by injecting nitrogen ions and platinum ions into the surface of the metal product in this order by ion implantation, thereafter forming a platinum film on the surface and further injecting platinum ions into the resulting surface by ion implantation.

5. A surface modifying process for a metal product



according to claim 4 wherein the nitrogen ion
implantation is effected in an amount of 1 to 5×10^{15}
ions/cm² at an acceleration voltage of 10 to 100 kev and
ionic current of 10 to 100 mA, and the platinum ion
5 implantation before and after forming the platinum film
is effected in an amount of 1 to 5×10^{17} ions/cm² at an
acceleration voltage of 10 to 200 kev and ionic current
of 10 to 100 mA.

6. A surface modifying process for a metal product
10 according to claim 4 or 5 wherein the platinum film to
be formed has a thickness of 0.1 to 0.5 μ m.

7. A process for modifying a surface of a metal
product which process is characterized by injecting
nitrogen ions, carbon ions and platinum ions into the
15 surface of the metal product in this order by ion
implantation, thereafter forming a platinum film on the
surface and further injecting platinum ions into the
resulting surface by ion implantation.

8. A surface modifying process for a metal product
20 according to claim 7 wherein the nitrogen ion
implantation is effected in an amount of 1 to 5×10^{15}
ions/cm² at an acceleration voltage of 10 to 100 kev and
ionic current of 10 to 100 mA, the carbon ion
implantation is effected in an amount of 1 to 3×10^{17}



ions/cm² at an acceleration voltage of 10 to 100 kev and ionic current of 10 to 100 mA, and the platinum ion implantation before and after forming the platinum film is effected in an amount of $1 \text{ to } 5 \times 10^{17}$ ions/cm² at an acceleration voltage of 10 to 200 kev and ionic current of 10 to 100 mA.

9. A surface modifying process for a metal product according to claim 7 wherein palladium ions are injected into the surface of the metal product by ion implantation after the nitrogen ion implantation and before the carbon ion implantation.

10. A surface modifying process for a metal product according to claim 9 wherein the palladium ion implantation is effected in an amount of $1 \text{ to } 5 \times 10^{15}$ ions/cm² at an acceleration voltage of 10 to 200 kev and ionic current of 10 to 50 mA.

11. A surface modifying process for a metal product according to any one of claims 7 to 10 wherein the platinum film to be formed has a thickness of 0.1 to 0.5 μm .

12. A surface modifying process for a metal product according to claim 1, 4 or 7 wherein the metal product is a die for preparing a glass product by press work.

