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(72) Inventors; and

(73) Inventors/Applicants (for US only): HIRAOKA, Yasushi; c/o Daido Steel Co., Ltd., Research & Development Center, 30, Daido-cho 2-chome, Minami-ku, Nagoya-shi, Aichi, 4578545 (JP).


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(54) Title: A METHOD FOR SURFACE TREATMENT OF A DIE-CASTING DIE

![Fig. 2](image-url)

(57) Abstract: The present invention is to provide a method for surface treatment that substantially provides no nitride compound layer that causes heat checks and abrasion to a die, while nitride is introduced in large quantities into the die internally, and as a result a die-casting die with excellent heat check resistance and excellent abrasion resistance can be produced. The method comprises a step of a nitriding process for forming on an aesthetic surface of the die-casting die a nitried layer that includes at least a compound layer composed of a compound by introducing gas containing at least ammonia gas to a heating furnace, a step of decomposing the compound by exhausting the ammonia gas from the heating furnace and for introducing ambient gas to the heating furnace, to carry out a thermal process to decompose the nitrogen compound, and a step of processing a shot peening process on the aesthetic surface of the die. The thickness of the compound layer contained in the nitried layer that is formed in the step of nitriding process is within the range of from 2/n to 7/n m.
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A METHOD FOR SURFACE TREATMENT OF A DIE-CASTING DIE

[TECHNICAL FIELD]

[0001] This invention relates to a method for the surface treatment of a die-casting die. It is provided by applying the compression residual stress in an aesthetic surface of the die-casting die using a shot-peening process.

[BACKGROUND OF THE INVENTION]

[0002] In a die-casting molding in which a casting cycle that includes pouring a molten metal, solidification, and stripping a cast product is repeated, small heat checks on an aesthetic surface of a die-casting die can be readily produced by a thermal history to be given by the casting cycles. Thus abrasions caused by mechanical contacts can be readily produced. The heat checks may develop into a crack or cracks to damage the die, and the abrasion may degrade the dimensional accuracy of the cast product. Therefore, to enhance heat check resistance and abrasion resistance to
extend a product's life, processes such as a surface nitriding process to enhance the hardness of the aesthetic surface of the die and a shot-peening process to provide the compression residual stress on the aesthetic surface are carried out.

[0003] The surface nitriding process in the die is often carried out by a gas nitriding process. The primary reasons for this are in the aspects of ease and the cost of the process. The gas nitriding process decomposes ammonia gas under a high temperature and diffuses the generated nitrogen from the aesthetic surface of the die to inside the die such that a diffusion-hardening layer is provided.

The shot-peening process at the die is mostly carried out by accelerating small spheres consisting of a ceramic or a hard metal less than 1 mm in diameter using a projection device to project them at the aesthetic surface of the die. On the aesthetic surface of the die, the compression residual stress is achieved based on the hardening process by means of the collisions of the small spheres.
[0004] For example, Patent Literature 1 discloses that the aesthetic surface of the die is first processed by the surface nitriding process to form a nitrogen diffusion-hardening layer and is then processed by the shot-peening process to yield a high compression residual stress on the surface of the diffusion-hardening layer. The surface nitriding process and the shot-peening process are carried out in combination such that the product lifetime of the die may be significantly extended.

[0005] It is known for the nitriding process that a compound layer lacking a plastic deformability is formed on the surface of the nitrogen diffusion-hardening layer. Because such a compound layer causes the heat checks to develop into a crack or cracks and abrasion due to a spailing, a nitriding process is proposed to prevent the formation of the compound layer, or to form it as thinly as possible.

[0006] For instance, Patent Literature 2 disclose a two-step process in which an ammonia gas nitriding process is first carried out in a range of relatively
low temperatures of 450-530 °C. The supply of the ammonia is then reduced or disrupted, while the nitrogen is internally diffused at a range of processing temperatures of 550-590 °C. Generally, with the ammonia gas nitriding process under the range of relatively low temperatures, the compound layer is thinly formed. However, the depth of the nitrogen diffusion layer also becomes shallow. Therefore, the nitrogen of the nitrogen diffusion layer is deeply diffused in the die to provide the thick nitrogen diffusion layer, while the thin compound layer is maintained.

[0007] Similarly, Patent Literature 3 disclose a two-step process in which an ammonia gas nitriding process is first carried out under reduced pressure at a temperature less than 570 °C. The supply of the ammonia is then reduced or disrupted, while the nitrogen is internally diffused at a range of processing temperatures of 570-650 °C. Patent Literature 3 describes that the nitride compound layer can be thin and in a non-porous state, while the depth of the nitride compound layer can be deeper than that of the nitrogen diffusion layer by the thermal process.
[SUMMARY OF THE INVENTION]

[THE PROBLEM TO BE SOLVED BY THE INVENTION]

[0009] As disclosed in Patent Literature 2 and 3, in the ammonia gas nitriding process to form the thin nitride compound layer, because actual
quantities of the nitrogen supplied to the die are little, the nitride compound layer cannot have a sufficient hardness when one makes an attempt in which the nitrogen of the nitrogen diffusion layer is further deeply diffused in the die by the thermal process.

[0010] The present invention was accomplished in view of such circumstances. The object of it is to provide a method for surface treatment that substantially provides no nitride compound layer that causes the heat checks or the abrasion to the die, while it can internally introduce large quantities of the nitride into a die. This results in producing a die-casting die with an excellent heat check resistance and an excellent abrasion resistance.

[MEANS TO SOLVE THE PROBLEM]

[0011] The inventors of the present invention found that the uppermost layer, composed of the nitride compound that is formed by various nitriding processes, such as a gas nitro carburizing process, a gas sulpho-nitriding process, and a plasma nitriding process, can be readily decomposed by a
thermal process. By a study about providing a method for manufacturing a
die that substantially provides no nitride compound layer to the die, the
inventors thought that the above decomposition generates nitrides such that
the quantities of the nitrides supplied to the die may be increased by
diffusing the generated nitrides in the die internally.

[0012] Accordingly, the method for the surface treatment of a die-casting die
that is provided by applying the compression residual stress in an aesthetic
surface of the die-casting die using a shot peening process, of the present
invention, comprises the step of nitriding processing for forming on an
aesthetic surface of the die-casting die a nitrided layer that includes at least
a compound layer composed of a nitrogen compound with a nitriding process,
for instance, gas nitro-carburizing, gas sulpho-nitriding, and plasma
nitriding, by introducing gas containing at least ammonia gas to a heating
furnace, the step of decomposing the compound for exhausting the ammonia
gas from the heating furnace and for introducing ambient gas to the heating
furnace, to carry out a thermal process to decompose the nitrogen compound,
and the step for shot-peening the aesthetic surface of the die. The thickness
of the compound layer contained in the nitrogen layer that is formed in the step of the nitriding process is within the range of from 2 μm to 7 pm.

[0013] With this method, the thickness of the nitrogen compound layer, which is formed with the nitriding process by introducing the gas containing at least ammonia gas to the heating furnace, is controlled to the predetermined thickness such that the nitrogen compound is decomposed in the step of decomposing the compound. As a result, no nitrogen compound layer is substantially provided. Thus the nitrogen is instead generated to increase quantities of the nitrogen to be supplied to the die such that a nitrogen diffusing layer having high hardness can be provided. Despite this, the substantially denied nitrogen compound layer should remain as the layer contains a significant number of voids to absorb and disperse the collision energies of the shots in the shot-peening process. However, the thickness of the nitrogen compound layer is also controlled to be at the predetermined thickness in the nitriding step such that the compression residual stress by the shot-peening process can be imparted on the nitrogen diffusion layer. Therefore, based on the high hardness and the high compression residual
stress, a die-casting die having excellent abrasion resistance and excellent heat check resistance can be produced.

[0014] In the above method, the step of decomposing the compound preferably carries out the thermal process at a temperature that is lower than that of the step of the nitriding process. In this case, higher hardness and higher compression residual stress can be imparted on the die-casting die such that the die having more excellent abrasion resistance and more excellent heat check resistance can be produced.

[BRIEF DESCRIPTION OF THE DRAWINGS]

[0015]

[Fig. 1] Fig. 1 is a perspective view of one specimen to be used with the embodiment of the method for surface treatment of the die-casting die of the present invention.

[Fig. 2] Fig. 2 indicates the steel classes and the conditions of the surface
treatment of the specimens disclosed in Fig. 1.

[Fig. 3] Fig. 3 illustrates one example of the heating and cooling examination equipment to be used with the embodiment of the method for surface treatment of the die-casting die of the present invention.

[Fig. 4] Figs. 4(a) and 4(b) are enlarged sectional views illustrating the changes of the specimen near the surface after the nitriding step (Fig. 4(a)) and after the compound decomposition step (Fig. 4(b)) in the method for surface treatment of the die-casting die of the present invention.

[Fig. 5] Figs. 5(a) and 5(b) are enlarged sectional views illustrating the changes in the nitrogen density of the specimen near the surface of Figs. 4(a) and 4(b).

[Fig. 6] Fig. 6 is a graph indicating the relationship between the thickness of the compound layer and the number of heat checks (HC) on the specimen on which the method for surface treatment of the die-casting die of the present
invention has been applied.

[Fig. 7] Fig. 7 is a graph indicating the relationship between the thickness of the compound layer and the residual stress on the specimen on which the step of shot peening of the method for surface treatment of the die-casting die of the present invention has been applied.

[Fig. 8] Fig. 8 is a photograph of the cross section of the specimen (the eleventh embodiment) after the nitriding step.

[THE EMBODIMENTS TO CARRY OUT THE INVENTION]

[0016] On the method for surface treatment of the die-casting die of the present invention, the details will be explained with reference to the result of the verification test as indicated in Figs. 1 to 8. In the verification tests, cylindrical specimens 1 (see Fig. 1) each corresponding to a die-casting die are prepared and various surface treatments are then carried out on them to evaluate them.
[0017] Cylindrical specimens 1 having an outer diameter Dl=15mm, an inner diameter D2 = 3mm, and a length L = 20mm are prepared. Each specimen 1 is machined from a round bar stock of Japanese Industrial Standards (JIS), the steel material of an alloy toll SKD 61 equivalency. Instead of the SKD 61 equivalency, the specimens 1 in the ninth embodiment and the tenth embodiment are machined from round bar stocks of JIS SKD 7 equivalency and a steel material of an alloy toll SKH51 equivalency. The steel classes of the embodiments and comparison examples are described and compiled in Fig. 2.

[0018] Each specimen 1 is then heated in a heating furnace while ammonia gas is introduced in the heating furnace such that the peripheral surface of the specimen is processed by a gas nitro-carburizing process (the nitriding step). Instead of the gas nitro-carburizing process, the specimen of the sixth embodiment is processed by a gas sulpho-nitriding process. Also, the specimens of both the seventh embodiment and the fifth comparison example are processed by a plasma-nitriding process. The types of nitriding processes,
the types of gasses, the temperatures, and the times of the embodiments and the comparison examples are described and compiled in Fig. 2.

[0019] The ammonia gas is then exhausted from the heating furnace, followed by which nitrogen is introduced as an atmospheric gas to the heating furnace, while the specimen is still thermal processed therein such that it is diffusion-processed. Thus, a nitrogen compound within a compound layer 2 (see Fig. 4) that is produced by the nitriding process, as described below, is completely dissolved (the step for decomposing the compound). The temperatures and the times of the diffusion process are also described and compiled in Fig. 2.

[0020] Spheres, for instance, each composed of an amorphous alloy of 0.05 mm-0.2 mm in diameter, are projected and shot-peened on the peripheral surface of the specimen 1 with projection pressure of 0.3 MPa (the step for shot-peening).

[0021] On the specimen 1 that has been processed by the above process, the
residual stress of the peripheral surface near the longitudinal center is measured.

[0022] Further, as illustrated in Fig. 3, each specimen 1 is tested by heating and cooling with examination equipment 20 repeatedly such that the heat check resistance is evaluated. More particularly, a small diameter portion 22a of a supporting member 22 of the examination equipment 20 is inserted through hole 1a in the specimen 1 such that the specimen 1 is pinched by means of a holder 23 from the top and bottom to fix it. The peripheral surface of the specimen 1 is heated from room temperature to 700 °C with a high frequency coil 21 in four seconds. Coolant water 24 is then jetted from a jet orifice (not shown) to cool the specimen 1 to room temperature in three seconds. The heated and cooled specimen 1 is then dried with an air blow for one second. This cycle of heating, cooling, and drying is repeated 1,000 times in total and the specimen 1 is removed from the examination equipment 20. The specimen 1 that is removed from the examination equipment 20 is cut near the longitudinal center in the plane that is perpendicular to the center axis thereof. The cut specimen 1 is then
mounted on a resin to mirror polish the cut surface of it. The cut surface of that specimen is observed using an optical microscope of 100 X magnification, to count the number of heat checks (HC) that appear on the peripheral surface of the specimen 1.

[0023] In addition, any pieces of the specimens 1 are removed from the heating furnace after the nitriding process described above to measure the thickness of the compound layer 2 (see Fig. 4) as below described. The specimen 1 that is removed from the heating furnace is cut near the longitudinal center in the plane that is perpendicular to the center axis thereof. The cut surface of the cut specimen 1 is then mirror polished. The polished cut surface is then observed using an optical microscope to measure the thickness of the compound layer 2.

[0024] In the nitriding process, as illustrated as in Figs. 4(a) and 5 (a), the activated nitrogen in a gas phase diffuses from the peripheral surface of the specimen 1 to the inside (a substrate) 4 to form a nitride layer 5 near the peripheral surface. The nitride layer 5 consists of a nitrogen compound layer
-2 that is the uppermost layer and a nitrogen diffusion layer 3 on the inside
the former. The compound layer 2 consists of a complex nitride of Fe or Cr,
and is an extremely fragile layer. It is noted that the growing rate of the
compound layer in the plasma-nitriding process is significantly lower than
that of the gas-nitriding process. The nitrogen diffusion layer 3 is a solid
solution layer of the nitrogen including a nitride that is dispersed and
precipitated.

[0025] In the diffusion process following the nitriding process described
above, the depth of the nitride layer 5 is increased, as illustrated in Figs. 4
(b) and 5 (b). More particularly, a flux in the nitrogen supplied to the
specimen 1 through the peripheral surface from the gas phase is degraded
such that the nitrogen of the nitrogen diffusion layer 3 primarily diffuses to
the inside of the specimen 1. In this time, if the nitrogen compound in the
compound layer 2 dissolves to yielded nitrogen, the yielded nitrogen also
diffuses to the inside of specimen 1. Because the density of the nitrogen
contained in the compound (see 3a in Fig. 5(a)) is significantly higher than
that contained in a solid solution (see 3b in Fig. 5(b)), e.g., the nitrogen
diffusion layer 3 of the nitrogen, the nitrogen diffusion layer 3 that contains significant large quantities of the nitrogen can be obtained (see 31 in Fig. 5(b)). In Fig. 5(b), 32 denotes the case in which only the nitrogen diffusion layer 3 provided by only the nitriding process is diffusion processed.

[0026] On the other hand, if the complex nitride in the compound layer 2 dissolves, a shrinkage in its volume results in a surface layer 2' that contains a large void volume. Such a surface layer 2' absorbs and dissipates the collision energies of the shots in the shot-peening process such that the formation of the compression residual stress is inhibited. Details of it are described below.

[0027] The results of the measurement described above will be now explained. Fig. 6 denotes the relationship between the thickness of the compound layer 2 and the number of the heat checks (HC) on the specimen after the repeated heating and cooling tests.

[0028] It is found that the number of heat checks can be decreased as the
thickness of the compound layer 2 is increased such that the heat check resistance may be enhanced. Indeed, forming a thin compound layer 2 of 1.5 pm in the first comparison example provides 597 heat checks and of 1.0 pm in the fifth comparison example provides 441 heat checks. In contrast, forming a thick compound layer 2 of 2μm to 7μm in the first through fourteenth embodiments provides significantly reduced numbers, 13 through 257, of heat checks.

Particularly, the heat check number significantly decreased in the eleventh embodiment in which the diffusion process (the heating treatment) is carried out at a temperature that is lower than that of the nitriding process. Therefore, it can be found that the heat treatment in the step for compound decomposition preferably is carried out at a temperature lower than that of the nitriding step.

[0029] Because the quantities of the nitrogen compound to be decomposed by the diffusion process can be increased as the thickness of the compound layer 2 is increased, as described above, the quantity of nitrogen in the nitrogen
diffusion layer 3 can be increased, the hardness after the diffusion process can be enhanced to improve the wear resistance, and the heat check resistance can be improved.

[0030] On the other hand, it can also be found that the number of heat checks rapidly increase as the thickness of the compound layer 2 is increased above a given thickness such that the heat check resistance may be significantly degraded. Indeed, forming thick compound layers 2 of 8.0 μm, 9.0 μm, and 10.0 pm in the first, second, and fourth comparison examples provide 706, 707, and 840 heat checks, respectively. They rapidly increased in comparison with those of the first through fourteenth embodiments.

[0031] In association with the above, Fig. 7 graphs the relationship between the thickness of the compound layer 2 and the residual stress to be given to the specimen 1 by the shot-peening. In Fig. 7, the compression stresses is expressed in negative values.

[0032] It can be found that the absolute value of the compression residual
stress may be increased as the thickness of compound layer 2 is increased. Indeed, forming thin compound layers 2 of 1.5 pm and 1.0 pm in the first and fifth comparison examples provides -965 MPa and -993 MPa of the compression residual stress. In contrast, forming a thick compound layer 2 of 2pm to 7pm in the first through fourteenth embodiments provides significant increased compression residual stress, -1350 MPa through -1755 MPa. They are significantly increased in comparison with those of the first and fifth comparison examples.

[0033] On the other hand, it can also be found that the absolute value of the compression residual stress may be rapidly degraded as the thickness of compound layer 2 is increased above a given thickness. Indeed, forming thick compound layers 2 of 8.0 pm, 9.0pm, and 10.0 pm in the second, third, and fourth comparison examples provide compression residual stress of -1298 MPa, -1251 MPa, and -938 MPa, respectively.

[0034] As described above, increasing the thickness of the compound layer 2 above a given thickness causes that the absolute value of the compression
residual stress is significantly decreased and thus the heat check resistance is significantly degraded. This is due to the surface layer 2' (see Fig. 4(b)) which contains large quantities of voids that are formed by decomposing the compound of the compound layer. More specifically, forming a thick compound layer 2 results in a thick surface layer 2' by the diffusion process such that the formation of the compression residual stress by shot-peening is rapidly inhibited, and thus the heat check resistance is significantly degraded.

[0035] Fig. 8 (a) is an optical microscope photograph of the cutting surface of the specimen 1 after the nitriding process in the eleventh embodiment. Fig. 8 (b) is an optical microscope photograph of the cutting surface of the specimen 1 after the diffusion process following the nitriding process in the eleventh embodiment. In the former, the compound layer 2 and the nitrogen diffusion layer 3 can be observed. In the latter, the increased thickness of the nitrogen diffusion layer 3 and the surface layer 2' that contains the voids blackly, especially near the nitrogen diffusion layer 3, by decomposing the compound, can be observed.
[0036] Based on the foregoing descriptions, constantly limiting the thickness of the compound layer 2 and thus the surface layer 2' that contains the voids, which remain after the compound is decomposed, provides the compression residual stress with an excellent property by shot-peening such that a die-casting die with an excellent heat check resistance can be obtained. Particularly, under the general conditions of the shot-peening process such as in the embodiments, the thickness of compound layer 2 (the surface layer 2' remaining after the compound is decomposed) to achieve this purpose is 2-7μm.

[0037] The relationships between the thickness of the compound layer 2 and the number of heat checks or the compression residual stress in Figs. 6 and 7 line up to the same plotted lines, regardless of differences between types of nitriding processes, for instance, gas nitro-carburizing, gas sulpho-nitriding, and plasma nitriding such as in the sixth and seventh embodiments. Also, they are regardless of differences between the steel materials of SKD61 equivalency material, SKD7 equivalency material, and SKH51 equivalency
material in the ninth and tenth embodiments. Namely, these results suggest that the method of the present invention can be applied regardless of the differences between types of nitriding processes and the differences between the common materials for the die.

[0038] As discussed above, the embodiments of the method for surface treatment of a die-casting die of the present invention comprises the step of a nitriding process for forming on the aesthetic surface of the die-casting die a nitrided layer that includes at least the compound layer composed of a nitrogen compound with the nitriding process, for instance, gas nitro-carburizing, gas sulpho-nitriding, and plasma nitriding, by introducing gas containing at least ammonia gas to the heating furnace, the step of decomposing the compound for exhausting the ammonia gas from the heating furnace and for introducing ambient gas to the heating furnace, to carry out the thermal process to decompose the nitrogen compound, and the step of the shot-peening for the shot-peening process on the aesthetic surface of the die. The thickness of the compound layer contained in the nitrogen layer that is formed in the step of the nitriding process is within the range of
from 2µm to 7µm.

[0039] The thickness of the nitrogen compound layer, which is formed with the nitriding process by introducing gas containing at least ammonia gas to the heating furnace, is kept at the predetermined thickness such that the nitrogen compound is decomposed in the step of decomposing the compound. At a result, no nitrogen compound layer is substantially provided and thus nitrogen is instead generated to increase the quantity of nitrogen to be supplied to the die such that a nitrogen diffusing layer having high hardness can be provided. Despite this, the substantially denied nitrogen compound layer remains as a layer containing a significant volume of voids to absorb and disperse the collision energies of the shots in the shot-peening process. However, the thickness of the nitrogen compound layer is also kept at the predetermined thickness in the nitriding step such that the compression residual stress of the shot-peening process can be imparted on the nitrogen diffusion layer. Therefore, the die-casting die having excellent abrasion resistance and excellent heat check resistance, based on high hardness and high compression residual stress, can be produced.
Although the representative embodiments and their variations of the present invention are described herein, the present invention is not intended to be limited to them. Those skilled in the art could have found various alternative embodiments and modifications without departure from the appended claims.

For example, although the foregoing explanation recites the specified shape and dimensions of each specimen, they are merely listed for convenience of explanation and are not intended to limit the present invention.

[BRIEF DESCRIPTIONS OF THE NUMERALS]

1 Specimen

2 Compound layer

3 Nitrogen diffusion layer

20 Examination equipment
[CLAIMS]

[Claim 1] A method for surface treatment of a die-casting die, which is provided by applying the compression residual stress in an aesthetic surface of the die-casting die using a shot-peening process, the method comprising the steps of:

- nitride processing for forming on an aesthetic surface of the die-casting die a nitrided layer that includes at least a compound layer composed of a nitrogen compound by introducing gas containing at least ammonia gas to a heating furnace;

- decomposing the compound by exhausting the ammonia gas from the heating furnace and for introducing ambient gas to the heating furnace to carry out a thermal process to decompose the nitrogen compound; and

- shot-peening processing on the aesthetic surface of the die;

wherein the thickness of the compound layer contained in the nitrogen layer that is formed in the step of the nitriding process is within the range of from 2μm to 7μm.
[Claim 2] The method for surface treatment of a die-casting die of claim 1, wherein the step of decomposing the compound carries out the thermal process at a temperature that is lower than that of the step of the nitriding process.
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<thead>
<tr>
<th>Steel Classes</th>
<th>Nitriding Processes</th>
<th>Temperature (°C)</th>
<th>Time (hr)</th>
<th>Types of Gasses</th>
<th>Thickness of Compound Layer (μm)</th>
<th>Diffusion Process Temperature (°C)</th>
<th>Time (hr)</th>
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<th>After-Shot-Peening</th>
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## A. CLASSIFICATION OF SUBJECT MATTER

INV. C23C8/24 C23C8/26 C23C8/28 C23C8/30 C23C8/32 C23C8/34 C23C8/36 C23C8/38

ADD.

According to International Patent Classification (IPC) and/or both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>A</td>
<td>US 2005/061402 Al (SANDUR AJITHKUMAR [IN]) 24 March 2005 (2005-03-24) claims 1-7; figure 1</td>
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<td>A</td>
<td>EP 1 229 143 A2 (MERITOR SUSPENSION SYSTEMS COM [US]) 7 August 2002 (2002-08-07) claims 1-15; figures 1,3</td>
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Further documents are listed in the continuation of Box C.

X See patent family annex.

* Special categories of cited documents:

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Date of the actual completion of the international search: 26 July 2011

Date of mailing of the international search report: 02/08/2011

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer: Chal aftris, Georgios
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<td>US 2005061402 AI</td>
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