

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 1 696 108 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

30.08.2006 Bulletin 2006/35

(51) Int Cl.:

F01L 3/02 (2006.01)

C22F 1/10 (2006.01)

B21J 9/08 (2006.01)

C22C 19/05 (2006.01)

(21) Application number: **06000958.6**

(22) Date of filing: **17.01.2006**

(84) Designated Contracting States:

**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IS IT LI LT LU LV MC NL PL PT RO SE SI
SK TR**

Designated Extension States:

AL BA HR MK YU

(30) Priority: **19.01.2005 JP 2005012030**

28.11.2005 JP 2005341574

(71) Applicants:

- **Daido Steel Co.,Ltd.**
Higashi-ku
Nagoya
Aichi 461-0005 (JP)
- **HONDA MOTOR CO., Ltd.**
Tokyo 107-8556 (JP)

(72) Inventors:

- **Ueta, Shigeki c/o Daido Steel Co.,Ltd.**
Minami-ku,Nagoya,
Aichi 457-8545 (JP)

- **Kurata, Seiji c/o Daido Steel Co.,Ltd.**

Minami-ku,Nagoya,
Aichi 457-8545 (JP)

- **Shimuzu, Tetsuya c/o Daido Steel Co.,Ltd.**

Minami-ku,Nagoya,
Aichi 457-8545 (JP)

- **Noda, Toshiharu c/o Daido Steel Co.,Ltd.**

Minami-ku,Nagoya,
Aichi 457-8545 (JP)

- **Tominaga, Katsuhiko**

Wako-shi,
Saitama,
351-0193 (JP)

- **Asami, Makoto**

Wako-shi,
Saitama,
351-0193 (JP)

(74) Representative: **Rupprecht, Kay et al**

Meissner, Bolte & Partner GbR

Postfach 86 06 24

81633 München (DE)

(54) **Heat resistant alloy for exhaust valves durable at 900°C and exhaust valves made for the alloy**

(57) An exhaust valve for automobile engines, which is durable at such a high temperature as 900°C, and exhibits high fatigue strength and high oxidation resistance is disclosed. The exhaust valve is made of a Ni-based alloy consisting essentially of, by weight %, C: 0.01-0.15%, Si: up to 2.0%, Mn: up to 1.0%, P: up to 0.02%, S: up to 0.01%, Co: 0.1-15%, Cr: 15-25%, one or two of Mo: 0.1-10% and W: 0.1-5% in such amount that Mo+1/2W: 3-10%, Al: 1.0-3.0%, Ti: 2.0-3.5%, provided that, by atomic %, Al+Ti: 6.3-8.5% and Ti/Al ratio: 0.4-0.8, and further, by weight %, B: 0.001-0.01%, Fe: up to 3%, and the balance of Ni and inevitable impurities by hot forging to give the form of an exhaust valve and subjecting to solid solution at 1000-1200°C and aging at 700-950°C

EP 1 696 108 A1

Description

TECHNICAL BACKGROUND

5 Field in the Industry

[0001] The present invention concerns exhaust valves for internal combustion engines, typically, automobile gasoline engines, which are durable at such a high temperature as 900°C and exhibit excellent fatigue properties and oxidation resistance. The invention concerns also a heat resistant alloy used as the material for the above-mentioned exhaust valves as well as the method of producing exhaust valves with the alloy.

Prior Art

[0002] As the material for the exhaust valves of automobile gasoline engines there has been widely used Ni-based heat resistant alloys such as NCF751 and NCF80A. To meet the demand for higher strength another Ni-based alloy (Japanese Patent Disclosure 61-119640) is suitable. This alloy was proposed by the applicant with a co-applicant, and contains, in addition to the suitable amounts of C, Si and Mn, by wt %, Cr: 15-25%, Mo+0.5W: 0.5-5.0%, Nb+Ta: 0.3-3.0%, Ti: 1.5-3.5%, Al: 0.5-2.5% and B: 0.001-0.02%. Further, there has been developed and disclosed another Ni-based alloy, (Japanese Patent Disclosure 05-059472), which contains, in addition to the suitable amounts of C, Si and Mn, by wt %, Co: 2.0-8.0%, Cr: 17.0-23.5%, Mo+0.5W: 2.0-5.5%, Al: 1.0-2.0%, Ti: 2.5-5.0%, B: 0.001-0.020% and Zr: 0.005-0.15%.

[0003] As is well known, for the purpose of keeping durability of exhaust valves it is necessary for the valves to withstand repeatedly given bending stress. The 10⁸-cycles fatigue strength of the above-mentioned newly developed alloys is, until the using temperature is up to 850°C, 245MPa or more. In the engines of the present days it is intended to realize combustion under near the stoichiometry, and this sometimes requires heat resistance of the valves at such a high temperature as 900°C. However, the fatigue strength of the known heat resistant alloys for exhaust valves decreases to be lower than 245MPa at 900°C, and the known alloys are dissatisfactory in regard to the strength as the material for the engines of the desired high performance

[0004] The inventors intended to provide a heat resistant alloy which satisfies the heat resistant condition of "10⁸-cycles fatigue strength at 900°C being 245MPa or more" and, as the results of investigation, noted that materials for disks and blades of gas turbines have heat resistance higher than that of conventional alloys for exhaust valves. Detailed study on the properties of the alloys for gas turbines revealed that they could be generally used as the materials for the exhaust valves. The noted heat resistant alloys are named "Waspaloy" and "Udimet 520" having the following typical alloy compositions (by weight %):

Waspaloy	Ni-19Cr-4.3Mo-14Co-1.4Al-3Ti-0.003B
Udimet	520 Ni-20Cr-6Mo-1W-12Co-2Al-3Ti-0.003B

[0005] The inventors further learned that the durability of these alloys differs in the gas turbines and the exhaust valves of engines and that it is necessity to confront with the difference. More specifically, high temperature creep property is required for the gas turbine material, while the high temperature fatigue strength is essential for the exhaust valve materials, and therefore, not only the alloy composition but also conditions for processing and heat treatment must be so chosen to obtain the desired properties.

[0006] From the view to achieve the high fatigue strength the inventors sought the ways for improving the properties of the gas turbine materials, and discovered that, by choosing the Mo- and W- contents to such a relatively high ranges as Mo+W: 3-10%, choosing the Co-content to a suitable amount, and arranging the amounts of Al and Ti to be, by atomic %, Al+Ti: 6.3-8.5%, and the Ti/Al ratio to be 0.4-0.8, the above requirement for the fatigue strength, 10⁸-cycles bending fatigue strength is 245MPa or more, can be satisfied. The inventors also discovered that addition of a small amount of Cu is effective for improving the oxidation resistance at 900°C.

SUMMARY OF THE INVENTION

[0007] The general object of the present invention is to provide, based on the above knowledge which the inventors obtained, a heat resistant alloy for exhaust valves which can be used at such a high temperature as 900°C and having high fatigue strength as well as oxidation resistance. The specific object of the present invention is to provide a heat resistant alloy having particularly high fatigue strength, in other words, an alloy exhibiting many more cycles of test at the same required strength level. To provide a method of producing exhaust valves with the present heat resistant alloy

is also the object of the present invention.

[0008] The heat resistant alloy for the exhaust valves achieving the above object, durable at the temperature of 900°C, according to the invention consists essentially of, by weight %, C: 0.01-0.15%, Si: up to 2.0%, Mn: up to 1.0%, P: up to 0.02%, S: up to 0.01%, Co: 0.1-15%, Cr: 15-25%, one or two of Mo: 0.1-10% and W: 0.1-5% in such amount as Mo+1/2W: 3-10%, Al: 1.0-3.0%, Ti: 2.0-3.5%, provided that, by atomic %, Al+Ti: 6.3-8.5% and Ti/Al ratio: 0.4-0.8, and further, by weight %, B: 0.001-0.01%, Fe: up to 3%, and the balance of Ni and inevitable impurities.

[0009] The method of producing the exhaust valves using the above-mentioned heat resistant alloy as the material comprises processing the material to form an exhaust valve consisting of a stem and a head by hot forging at 1000-1200°C, and subjecting the processed intermediate product to solid solution treatment at 1000-1200°C, and aging treatment at 700-950°C.

PREFERRED EMBODIMENTS OF THE INVENTION

[0010] The heat resistant alloy for exhaust valves according to the invention may contain, in addition to the above-mentioned basic alloy components, by weight %, one or more of V: 0.5-1.5%, Nb: 0.5-1.5% and Ta: 0.5-1.5% in such amount that, by atomic %, Al+Ti+Nb+TA+V: 6.3-8.5%. The strength of the alloy will be enhanced by addition of the element or elements.

[0011] The heat resistant alloy for exhaust valves of the invention may further contain, in addition to the above mentioned components, one or more of Mg: 0.001-0.03%, Ca: 0.001-0.03%, Zr: 0.001-0.1% and REM: 0.001-0.1%. By adding the element or elements, hot workability of the alloy will be improved. REM improves, in addition to this effect, oxidation resistance of the alloy.

[0012] The present heat resistant alloy for exhaust valves may further contain Cu: 0.01-2%. Addition of Cu enhances the oxidation resistance of the product valves.

[0013] The following explains the reasons for selecting the above-described composition of the heat resistant alloy for the exhaust valves according to the invention in the order of the essential elements and the optionally added elements. C: 0.01-0.15%

[0014] Carbon combines with Ti, Nb and Ta to form MC carbides, and with Cr, Mo and W to form $M_{23}C_6$, M_6C carbides, which are useful for preventing coarsening of the grains and enhancing the grain boundaries. To obtain these merits at least 0.01% of carbon is necessary. Too much carbon forms too large amount of carbides, which lowers the workability at forming the valves, the toughness and the ductility of the alloy. Thus, 0.15% is the upper limit of C-content. Si: up to 2.0%

[0015] Silicon is an element used as the deoxidizing agent at melting and refining the alloy, and may be used if necessary. Silicon is also useful for increasing oxidation resistance of the alloy. However, too high a content of Si lowers the toughness and the workability of the alloy, and the addition should be in an amount up to 2.0%.

Mn: up to 1.0%

[0016] Manganese also takes the role of deoxidizing agent like silicon, and may be added if necessary. Too much addition damages the workability and the high temperature oxidation resistance of the alloy, and therefore, the amount of addition should be chosen in the range up to 1.0%.

P: up to 0.02%, S: up to 0.01%

[0017] Phosphor and sulfur are inevitable impurities of the Ni-alloy of the invention and undesirable, because they lower the hot workability of the alloy. Particularly, the practical range of processing conditions of hot working of the alloy of the invention is, due to the low Ni-content, narrow. From the view to ensure the hot workability the allowable limits of P and S are determined as above.

Co: 0.1-15%

[0018] Cobalt stabilizes γ phase at high temperature and strengthen the matrix to contribute to improvement of fatigue strength. On the other hand, addition of much amount of cobalt results in increased costs, and moreover, excess cobalt makes the austenite phase unstable. Thus, amount of adding cobalt is in the above range, preferably 2-15%, more preferably, 8-14%.

Cr: 15-25%

[0019] Chromium is essential for increasing the heat resistance of the alloy, and the necessary amount of addition for this purpose is at least 15%. Because addition of Cr exceeding 20% causes precipitation of σ -phase, which results in decrease in toughness and high temperature strength, an amount up to 25% should be chosen. Preferable amount of Cr is in a relatively low range, 15-20%.

One or both of Mo: 0.1-10% and W: 0.1-5%, provided that

Mo+0.5W: 3-10%

[0020] Both molybdenum and tungsten are the elements which improve the high temperature strength of the alloy by enhancing solid solution of the matrix, and therefore, important components for high fatigue strength at 900°C intended by the inventors. To achieve this purpose both the elements are added in the respective amounts of at least 0.1%.

Addition of large amounts causes increased costs and decreased workability, and thus, the upper limits as above are given. Preferable amount of Mo is usually in the higher range of 5-10%. However, excess addition is not advantageous due to decreased oxidation resistance.

Al: 1.0-3.0%, Ti: 2.0-3.5%

[0021] Aluminum is an important element in combining with nickel to form γ' -phase. At an Al-content less than 1.0% precipitation of γ' -phase is so insufficient that the desired high temperature strength cannot be obtained. On the other hand, at an Al-content exceeding 3.0% hot workability of the alloy is low.

[0022] Titanium also combines with nickel to form γ' -phase which is useful for improving the high temperature strength. In case where the Ti-content is so small as less than 2.0%, solid solution temperature of the γ' -phase becomes low, and as the result, sufficient high temperature strength cannot be obtained. Addition of Ti to such a large amount as more than 3.5% lowers the workability, and causes precipitation of η -phase (Ni_3Ti), which lowers the high temperature strength and the toughness of the alloy. Also, hot processing of the alloy becomes difficult.

By atomic %, Al+Ti: 6.3-8.5%; Ti/Al ratio: 0.4-0.8

[0023] As seen from the above, the amount of Al+Ti(+Nb) is a measure for the amount of γ' -phase at 900°C. In case where the amount of Al+Ti(+Nb) is small, the fatigue strength of the alloy is low, while in case where the amount is large, hot processing becomes difficult. This is the reason why the range, by atomic %, 6.3-8.5% is chosen.

[0024] The Ti/Al ratio is an important factor for stabilizing the γ' -phase at 900°C and increasing the fatigue strength. At such a low value of the ratio as less than 0.4, aging effect is so small that the sufficient strength may not be obtained. On the other hand, such a high value as more than 0.8 causes precipitation of the η -phase and the strength of the alloy will be low. Preferable ratio in the above range is 0.6-0.8, in which the intended improvement in the fatigue strength will be effectively achieved.

B: 0.001-0.01%

[0025] Boron contributes to improvement in the hot workability of the alloy, and further, improves the fatigue strength by segregating at the grain boundaries to enhance the strength of the grain boundaries. Thus, B is added in an amount of 0.001% or more at which the above effects can be obtained. Excess addition of B lowers the melting point of the matrix to damage the hot workability, and therefore, addition amount should be up to 0.01%.

Fe: up to 3%

[0026] Iron is a component which, depending on the choice of the materials, inevitably comes into the product alloy. If the Fe-content is large, then the strength of the alloy will be low, and therefore, a lower Fe-content is preferable. As the permissible limit the above 3% is given. It is recommended to limit the Fe-content to be less than 1%, which can be done by selecting the materials.

One or more of V: 0.2-1.0%, Nb: 0.5-1.5% and Ta: 0.5-1.5%, by atomic %, Al+Ti+Nb+Ta+V: 6.3-8.5%

[0027] Niobium, tantalum and vanadium all combine with Al and Ni to strengthen the γ' -phase. Vanadium also contributes to solution hardening. If these effects are expected, it is recommended to add one or more of these elements in an amount or amounts of the above lower limit or more. Because excess content or contents will decrease the toughness of the alloy, the addition should be made in the amount or amounts up to the respective upper limits and not exceeding the limited total amount.

One or more of Mg: 0.001-0.03%, Ca: 0.001-0.03%, Zr: 0.001-0.1% and REM: 0.001-0.1%

[0028] Addition of these elements improves the hot workability of the alloy. Zirconium also exhibits the effect of enhancing the grain boundaries by segregating at the grain boundaries. REM (Rare earth metals) improve, not only the hot workability, but also the oxidation resistance of the alloy. In order to obtain these merits it is recommended to add the element or elements in an amount or amounts of at least the lower limit or limits. Excess contents makes the temperature at which melting of the alloy begins lower, resulting in the lowered hot workability, and therefore, addition should be so made that the amount or amounts of the element or elements do not exceed the respective upper limits.

Cu: 0.01-2%

[0029] As mentioned above, addition of copper increases oxidation resistance of the alloy and improves the durability of the product valves. Addition in the amount of 0.01% or more is recommended. Excess addition of Cu results in decreased hot workability, and therefore, addition must be up to 2.0%

[0030] The heat resistant alloy for exhaust valves according to the present invention exhibits, after being subjected to the solution treatment and the aging, 10^8 -cycles fatigue strength at 900°C of 245MPa or more, and the weight increase after being subjected to oxidation test by keeping at 900°C for 400 hours is 5mg/cm² or less. The exhaust valves made of the present alloy can withstand against such a high temperature as 900°C that the valves made of the conventional materials cannot withstand. Thus, the valves have high durability given by high fatigue strength and high oxidation resistance, and meet the demand for increased performance of automobile engines.

EXAMPLES

[0031] Ni-based alloys having the alloy compositions shown in Table 1 (Working Examples) and Table 2 (Control

Examples) were prepared in a 50kg HF-induction furnace and cast into ingots. The Ni-based alloys prepared for the comparison are those used or proposed for the material of the conventional exhaust valves, which are of the following steel marks.

Control 1: NCF751

Control 2: NCF80

Control 3: Ni-based alloy disclosed in Japanese Patent

Disclosure 61-119640

[0032] Control 4: Ni-based alloy disclosed in Japanese Patent

Disclosure 05-059472

[0033] The respective ingots were forged and rolled to rods of diameter 16mm. The rods were subjected to solid solution treatment of heating at 1050°C for 1 hour followed by water quenching, and aging by heating at 750°C for 4 hours followed by air cooling. The obtained materials were subjected to tensile test and rotary bending fatigue test at 900°C and continuous oxidation test for 400 hours. The results are shown in Table 3 (Working Examples) and Table 4 (Control Examples) together with the values of Ti/Al ratios and atomic % of Al+Ti.

TABLE 1 Alloy Composition (Working Examples Weight %, balance Ni)

No.	C	Si	Mn	P	S	Cr	Co	Mo	W	Al	Ti	Nb+ Ta	B	Zr, V, Mg, Ca	Fe	Cu	Mn+ 1/2W
A	0.03	0.23	0.56	0.005	0.003	18.3	13.1	4.4	—	1.9	2.6	—	0.004	—	0.1	—	4.4
B	0.05	0.05	0.09	0.004	0.002	16.1	5.8	6.3	—	2.1	2.3	1.3	0.003	Mg 0.003 Ca 0.002	1.3	—	6.3
C	0.04	0.13	0.24	0.003	0.001	20.5	9.9	5.6	1.7	1.8	2.1	0.9	0.003	Zr 0.03 Mg 0.003Ca 0.001	0.7	—	6.5
D	0.08	0.18	0.15	0.001	0.001	15.8	12.0	4.9	—	1.8	2.4	—	0.005	—	0.1	0.9	4.9
E	0.03	0.07	0.12	0.002	0.001	19.2	14.3	3.5	2.1	2.3	2.6	0.6	0.002	Zr 0.03 V 0.2 Mg 0.002	0.3	—	4.6
F	0.06	0.10	0.21	0.003	0.002	22.4	8.7	2.6	1.5	2.7	2.1	—	0.004	Zr 0.05	0.2	—	3.4
G	0.05	0.26	0.18	0.004	0.001	17.6	3.5	5.4	—	1.6	2.2	1.1	0.003	Ca 0.002	0.5	1.3	5.4
H	0.04	0.14	0.20	0.002	0.003	21.7	8.9	2.3	2.6	1.8	2.2	0.5	0.003	Zr 0.06 Mg 0.003	1.6	—	3.6
I	0.07	0.09	0.17	0.001	0.001	19.0	10.1	1.8	2.6	2.1	2.0	—	0.003	V 0.3	0.9	—	3.1
J	0.04	0.11	0.08	0.003	0.002	18.9	4.6	3.7	1.3	2.2	2.5	0.8	0.004	Zr 0.05 Mg 0.005	0.7	—	4.4
K	0.03	0.22	0.16	0.002	0.001	23.1	13.6	5.5	—	2.3	3.1	—	0.005	Ca 0.002	1.0	—	5.5
L	0.05	0.15	0.13	0.002	0.001	20.2	8.2	6.1	0.9	1.8	2.3	—	0.003	Mg 0.003 REM 0.002	0.5	—	6.6

TABLE 2 Alloy Composition (Control Examples, Weight %, Balance Ni)

No.	C	Si	Mn	P	S	Cr	Co	Mo	W	Al	Ti	Nb+ Ta	B	Zr, V, Mg, Ca	Fe	Cu	Mo+ 1/2W
1	0.05	0.15	0.17	0.002	0.001	16.3	—	—	—	1.2	2.5	—	0.003	—	7.1	—	—
2	0.06	0.23	0.18	0.003	0.002	20.5	—	—	—	1.4	2.6	—	0.004	—	0.6	—	—
3	0.05	0.12	0.16	0.002	0.002	18.7	—	1.2	1.4	1.4	2.5	—	0.005	—	3.2	—	1.9
4	0.08	0.05	0.09	0.002	0.001	19.6	—	0.9	—	1.9	2.6	1.0	0.005	—	5.1	—	0.9

Table 3 Test results, Working Examples

No.	Ti/Al Atomic ratio	Al+Ti+ (Nb+Ta+V) (Atomic %)	900°C Tensile Strength (MPa)	900°C 10 ⁸ -cycles Fatigue Strength (MPa)	900°Cx400hours Weight increase by oxidation (mg/cm ²)
A	0.77	7.05	582	270	1.4
B	0.62	8.01	609	284	1.7
C	0.66	6.93	571	265	1.3
D	0.75	6.64	548	250	1.8
E	0.64	8.42	620	294	1.3
F	0.44	8.05	583	265	1.2
G	0.75	6.26	624	294	1.6
H	0.69	6.67	546	250	1.2
I	0.54	6.91	557	250	1.4
J	0.64	8.09	585	274	1.4
K	0.76	8.41	627	299	1.1
L	0.72	6.56	556	252	1.4

Table 4 Test results, Control Examples

No.	Ti/Al Atomic ratio	Al+Ti+ (Nb+Ta+V) (Atomic %)	900°C Tensile Strength (MPa)	900°C 10 ⁸ -cycles Fatigue Strength (MPa)	900°Cx400hours Weight increase by oxidation (mg/cm ²)
1	1.18	5.41	333	89	1.7
2	1.05	5.91	380	104	1.4
3	1.01	5.89	436	142	1.5
4	0.77	7.55	479	196	1.5

Claims

1. A heat resistant alloy for exhaust valves, which are durable at 900°C, consisting essentially of, by weight %, C: 0.01-0.15%, Si: up to 2.0%, Mn: up to 1.0%, P: up to 0.02%, S: up to 0.01%, Co: 0.1-15%, Cr: 15-25%, one or two of Mo: 0.1-10% and W: 0.1-5% in such an amount as Mo+1/2W: 3-10%, Al: 1.0-3.0%, Ti: 2.0-3.5%, provided that, by atomic %, Al+Ti: 6.3-8.5% and Ti/Al ratio: 0.4-0.8, and further, by weight %, B: 0.001-0.01%, Fe: up to 3%, and the balance of Ni and inevitable impurities.
2. The heat resistant alloy for exhaust valves according to claim 1, wherein the alloy further contains, by weight %, one or more of V: 0.2-1.0%, Nb: 0.5-1.5% and Ta: 0.5-1.5% in such an amount as, by atomic %, Al+Ti+Nb+Ta+V: 6.3-8.5%.
3. The heat resistant alloy for exhaust valves according to claim 1 or claim 2, wherein the alloy further contains, by weight %, one or more of Mg: 0.001-0.03%, Ca: 0.001-0.03%, Zr: 0.001-0.1% and REM: 0.001-0.1%.
4. The heat resistant alloy for exhaust valves according to one of claims 1 to 3, wherein the alloy further contains, by weight %, Cu: 0.01-2%.
5. The heat resistant alloy for exhaust valves according to one of claims 1 to 4, wherein the alloy exhibits, after being treated by solid solution and aging, 10⁸-cycles fatigue strength at 900°C of 245MPa or more, and the weight increase

after being subjected to oxidation test by keeping at 900°C for 400 hours is 5mg/cm² or less.

- 5
6. A method of producing an exhaust valve, which comprises processing the alloy according to one of claims 1 to 4 by hot forging at 1000° to 1200°C to form an intermediate product having the form of an exhaust valve consisting of a stem and a head, and then, subjecting the intermediate product to solid solution treatment by heating at 1000° to 1200°C, and aging treatment by heating to 700° to 950°C.
- 10
7. A method of producing an exhaust valve, which comprises consolidating a stem-tip made of a martensitic or austenitic heat resistant steel to the stem end of the intermediate product of the exhaust valve made by the method according to claim 6 by friction bonding.

15

20

25

30

35

40

45

50

55



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 06 00 0958

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
D,A	PATENT ABSTRACTS OF JAPAN vol. 010, no. 310 (C-379), 22 October 1986 (1986-10-22) & JP 61 119640 A (HONDA MOTOR CO LTD; others: 01), 6 June 1986 (1986-06-06) * abstract * & US 4 871 512 A (TAKAGI ET AL) 3 October 1989 (1989-10-03) -----	1-7	INV. F01L3/02 B21J9/08 C22F1/10 C22C19/05
D,A	PATENT ABSTRACTS OF JAPAN vol. 017, no. 373 (C-1083), 14 July 1993 (1993-07-14) & JP 05 059472 A (HITACHI METALS LTD), 9 March 1993 (1993-03-09) * abstract * -----	1-7	
A	US 6 139 660 A (NAGASHIMA ET AL) 31 October 2000 (2000-10-31) * the whole document * -----	1,6	
A	EP 0 889 207 A (DAIDO STEEL COMPANY LIMITED) 7 January 1999 (1999-01-07) * claim 2; table 1 * -----	1,6	TECHNICAL FIELDS SEARCHED (IPC)
A	US 2002/195175 A1 (ISHIDA KIYOHITO ET AL) 26 December 2002 (2002-12-26) * paragraph [0063]; claim 1; table 1 * -----	1,2,6	F01L B23P B21K B21J C22C C22F
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 11 May 2006	Examiner Clot, P
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document</p>			

1

EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 06 00 0958

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

11-05-2006

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
JP 61119640	A	06-06-1986	CA 1255927 A1	20-06-1989
			DE 3540287 A1	22-05-1986
			GB 2167440 A	29-05-1986
			JP 1488534 C	23-03-1989
			JP 63039654 B	05-08-1988
			US 4871512 A	03-10-1989

US 4871512	A	03-10-1989	CA 1255927 A1	20-06-1989
			DE 3540287 A1	22-05-1986
			GB 2167440 A	29-05-1986
			JP 1488534 C	23-03-1989
			JP 61119640 A	06-06-1986
			JP 63039654 B	05-08-1988

JP 05059472	A	09-03-1993	NONE	

US 6139660	A	31-10-2000	NONE	

EP 0889207	A	07-01-1999	AT 230066 T	15-01-2003
			DE 69810197 D1	30-01-2003
			DE 69810197 T2	09-10-2003
			JP 11022427 A	26-01-1999
			US 6193822 B1	27-02-2001

US 2002195175	A1	26-12-2002	JP 2002363674 A	18-12-2002
