(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 695 811 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
07.02.1996 Bulletin 1996/06

(51) Int Cl.[6]: C22C 37/10

(21) Application number: 95305233.9

(22) Date of filing: 26.07.1995

(84) Designated Contracting States:
DE FR GB

(30) Priority: 05.08.1994 JP 184636/94
20.07.1995 JP 205078/95

(71) Applicant:
TOYOTA JIDOSHA KABUSHIKI KAISHA
Aichi-ken (JP)

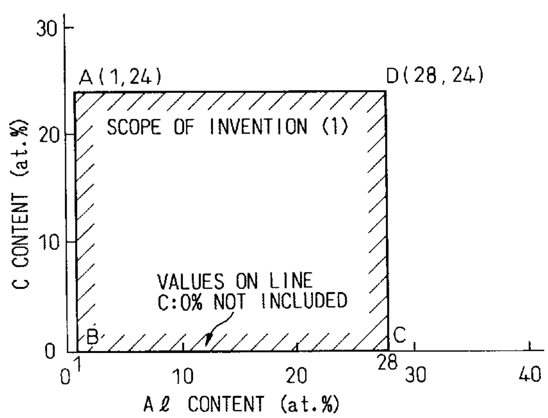
(72) Inventors:
- Shamoto, Hiroyuki
Toyota-shi, Aichi (JP)
- Morikawa, Takashi
Toyota-shi, Aichi (JP)

(74) Representative:
Ben-Nathan, Laurence Albert et al
London W1M 8AH (GB)

(54) High heat-resisting iron-base alloy

(57) A high heat-resisting iron-base alloy characterized by having a composition which is represented by the general formula: $Fe_xAl_yC_z$, wherein y and z are, in terms of atomic %, 1% ≦ y(at.%) ≦ 28% and 0% < z (at.%) ≦ 24%, respectively, with x constituting the balance, and falls within the area formed by connecting points A, B, C, and D shown in Fig. 1.

Fig.1



EP 0 695 811 A1

Description

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to an Fe-Al-C-base alloy and more particularly to an iron-base alloy, having excellent heat resistance, for use at high temperatures.

2. Prior Art

An ever-increasing tendency toward the use of heat resisting materials in an exhaust system and other systems of automobiles under severer service conditions in recent years has necessitated the prevention of high temperature deformation and a lowering in tensile strength of these materials in higher temperature environments. Further, these materials should have such properties as high-temperature strength, small creep elongation, and excellent thermal fatigue resistance and impact resistance. For this reason, expensive alloying elements, such as Cr and Ni, have hitherto been used in the art.

Such high heat resisting iron-base materials known in the art include, for example, SCH-base heat resisting steel casting materials (JIS G5122) and FCDA-base nodular graphite austenitic iron castings (JIS G5510). When these materials are classified according to heat resistance properties, high-silicon nodular graphite cast iron can be first mentioned. For this material, since the transformation temperature is so low that it is difficult to use the material in a higher temperature region of 800°C or above. For this reason, a ferrite cast steel has been used as a material for use in this higher temperature region. Cr incorporated in an amount of not less than 15% in this material, however, is expensive. Further, austenitic cast iron can also be mentioned as a material for use at high temperatures. In this material as well, Cr or Ni, which is an expensive alloying element, is used.

On the other hand, in recent years, lightweight and high melting point of an FeAl intermetallic compound have attracted attention, and the development of an alloy system of this compound has been put forward. For example, Japanese Unexamined Patent Publication (Kokai) No. 3-226547, which has been filed by the applicant of the present invention, discloses, as a high toughness material, an Fe-Al-base intermetallic compound material having an Al content of 36.8 to 49.4 at.%. As with the conventional heat resisting materials, this intermetallic compound material contains Cr from the viewpoint of improving the toughness.

Regarding the prior art in this field, Japanese Unexamined Patent Publication (Kokai) No. 56-58950 discloses an alloy, having an Al content of 0.72 to 18.7 at.%, for a heat treatment roll having an improved pickup property. Japanese Unexamined Patent Publication (Kokai) No. 57-126949 discloses an alloy, having an Al content of 17 to 32.7 at.%, as a vibration control alloy which causes regular-irregular transformation. In addition, Japanese Unexamined Patent Publication (Kokai) No. 57-203750 discloses an alloy, having an Al content of 0.2 to 7.4 at.% and a C content of 1.83 to 8.3 at.%, as a magnetic material for a composite of magnetic material/non-magnetic material, Japanese Unexamined Patent Publication (Kokai) No. 62-270452 discloses an alloy, having an Al content of 13.5 to 37.3 at.% and a C content of 0.004 to 3.2 at.%, for a carbon fiber-reinforced concrete structure with a reinforcing bar being embedded therein, and Japanese Unexamined Patent Publication (Kokai) No. 6-25800 discloses an alloy, having an Al content of 25 to 50 at.%, for a high-strength and abrasion-resisting material with a carbide being dispersed therein. None of the above known techniques, however, disclose an Fe-Al-C ternary alloy as at least heat resisting material.

It is reported that, in general, in terms of a phase diagram of an alloy, for an Fe-Al-base alloy, ferrite is formed when the Al content is not more than 54 at.%, while for an Fe-Al-C ternary alloy, the percentage of graphitization increases with increasing the Al content until the Al content reaches about 5 at.% and decreases with further increase in the Al content and, thereafter, a carbide phase and a ferrite phase having relatively high hardness are formed.

Regarding the heat resistance of Al cast iron, it is known that, by virtue of a strong Al_2O_3 film formed by Al incorporated on the surface of the Al cast iron, the Al cast iron does not permit the penetration of oxygen thereinto, has excellent oxidation resistance at a high temperature, is less likely to cause growth of a carbide, and has excellent heat resistance (see, for example, "Tokushu Chutetsu (Special Cast Iron)," 3rd edition, published by Nikkan Kogyo Shimbun, Ltd., 1960).

The above conventional materials, however, do not have satisfactory heat resistance at higher temperatures and, further, have problems associated with the production thereof. For this reason, the development of an iron-base material, which contains no expensive alloying elements, such as Cr and Ni, is less expensive, and has excellent high-temperature heat resistance, has been desired in the art.

SUMMARY OF THE INVENTION

An object of the present invention is to study an Fe-Al-C-base alloy as a ternary alloy with a view to solving the above problems of an Fe-Al-base alloy and to provide a high heat-resisting iron-base alloy having lowered average coefficient of linear expansion, enhanced transformation temperature, and excellent tensile strength.

Another object of the present invention is to provide a high heat-resisting iron-base alloy mainly consisting of Fe, Al, and C alone without use of conventional expensive alloying elements, such as Cr and Ni, which high heat-resisting iron-base alloy is inexpensive and has improved mechanical properties equal or superior to the conventional alloys.

A further object of the present invention is to provide a high heat-resisting iron-base alloy through study of ingredients capable of reducing the problem associated with the production of an Fe-Al-base alloy, particularly improving the castability.

The above objects can be attained by a high heat-resisting iron-base alloy mentioned as the following.

(1) A high heat-resisting iron-base alloy is characterized in essentially consisting of a composition, in terms of atomic %, which is represented by the general formula: $Fe_xAl_yC_z$, wherein y and z are $1\% \leqq y(\text{at.\%}) \leqq 28\%$, and $0\% < z(\text{at.\%}) \leqq 24\%$, respectively, with x being the remainder.

(2) The high heat-resisting iron-base alloy according to item (1), wherein y and z fall within the area formed by connecting points A(1, 24), B(1, 0), C(28, 0) and D(28, 24) shown in Fig. 1, provided that for the values on line C: 0% is excluded.

(3) The high heat-resisting iron-base alloy according to item (1), wherein y and z further satisfy the inequalities (1) to (4) hereunder;

$$5y - 8z \geqq 25 \text{ (here, } z < 5 \text{ at.\%)} \quad (1)$$
$$5y - 2z \geqq 55 \text{ (5 at.\%} \leqq z < 10 \text{ at.\%)} \quad (2)$$
$$y \geqq 15 \text{ (10 at.\%} \leqq z < 15 \text{ at.\%)} \quad (3)$$
$$y + 3z \geqq 60 \text{ (15 at.\%} \leqq z) \quad (4).$$

(4) The high heat-resisting iron-base alloy according to item (1), wherein y and z fall within the area formed by connecting points A(1, 24), E(1, 19), F(15, 15), G(15, 10), H(13, 5), I(5, 0), C(28, 0) and D(28, 24) shown in Fig. 2, provided that for the values on line C: 0% is excluded.

(5) The high heat-resisting iron-base alloy according to item (1), wherein y and z further satisfy the inequality (5) hereunder;

$$z \leqq 12 \text{ at.\%} \quad (5).$$

(6) The high heat-resisting iron-base alloy according to item (1), wherein y and z fall within the area formed by connecting points J(1, 12) B(1, 0), C(28, 0) and K(28, 12) shown in Fig. 3, provided that for the values on line C: 0% is excluded.

(7) The high heat-resisting iron-base alloy characterized in essentially consisting of a composition, in terms of atomic %, which is represented by the general formula: $Fe_xAl_ySi_{z1}C_{z2}$, wherein y, z_1 and z_2 fall within the area formed by connecting points A(1, 24), J(1, 12), L(8, 10), M(7, 5), B(1, 0), C(28, 0) and D(28, 24) shown in Fig. 4, in which $z_{total} = z_2 + 0.75z_1$, and $0.2 \text{ at.\%} \leqq z_1 \leqq 10 \text{ at.\%}$.

(8) The high heat-resisting iron-base alloy according to any one of items (1) to (7) further comprising a graphitizer.

(9) The high heat-resisting iron-base alloy according to item (8) further comprising 0.2 to 2.0 at.% of at least one element selected from the group of Ti, V, Cr, Ta, W, Nb and Mn as the graphitizer.

(10) The high heat-resisting iron-base alloy according to item (8) further comprising 0.2 to 2.0 at.% of one or both of B and Zr as the graphitizer.

(11) The high heat-resisting iron-base alloy according to item (8) further comprising 0.01 to 0.2 at.% of P as the graphitizer.

(12) The high heat-resisting iron-base alloy according to item (8) further comprising 0.2 to 5.0 at.% of one or both

of Ni and Cu as the graphitizer.

(13) The high heat-resisting iron-base alloy according to any one of items (1) to (12) further comprising an element or a compound for refining.

(14) The high heat-resisting iron-base alloy according to item (13) further comprising 0.1 at.% or more of at least one selected from the group of Ti, V, Cr, Ta, B, Mo, Sm, Sn, FeB, TaB_2, TiB_2, HfC, TiC, Ag, Ca, Co, Ge, Hf, P, Yb, B_4C, NbB_2, Mo_2C, VC, Cr_2N, Fe_3N, Fe_4N, TiN and VN as the element or the compound for refining.

(15) The high heat-resisting iron-base alloy according to any one of items (1) to (14) further comprising an element or a compound for improving ductility.

(16) The high heat-resisting iron-base alloy according to item (15) further comprising 0.1 at.% or more of at least one selected from the group of Ce, Er, Gd, Nd, Dy, La, Pr, Y, $BaAl_4$ and Fe_4N as the element or the compound for improving ductility.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a diagram showing the scope of the first invention in terms of the relationship between the C content and the Al content.

Fig. 2 is a diagram showing the scope of the second invention in terms of the relationship between the C content and the Al content.

Fig. 3 is a diagram showing the scope of the third invention in terms of the relationship between the C content and the Al content.

Fig. 4 is a diagram showing the scope of the fourth invention in terms of the relationship between the C + 0.75Si amount and the Al content.

Figs. 5(a) to 5(c) are metallic structure photographs of Fe-10 at.% Al-2 at.% C alloy showing the effect of the refining element according to thirteenth and fourteenth claims, Fig. 5(a) shows without addition, Fig. 5(b) shows with addition of 0.8 at.% TiB_2, Fig. 5(c) shows with addition of 1.9 at.% TiB_2.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The alloy of the first invention has a low coefficient of thermal expansion and creates neither significant strain nor significant stress even under high temperature environments and, hence, can be an excellent heat resisting material.

The alloy of the second invention has a high transformation temperature and creates neither significant expansion nor significant shrinkage even under high temperature conditions and, hence, can be an excellent heat resisting material.

The alloy of the third invention has a low coefficient of thermal expansion and, in addition, high tensile strength and, hence, can be an excellent heat resisting material.

The reasons for the limitation of ingredients specified in the present invention will now be described.

In the first invention, when the Al content is less than 1 at.%, the oxidation resistance becomes unsatisfactory, while when it exceeds 28 at.%, the coefficient of thermal expansion becomes large, making it difficult to use the alloy as a heat resisting material. When the C content exceeds 24 at.%, the melting point of the alloy is high, making it very difficult to melt the alloy. The lower limit of the C content is more than 0 at.% exclusive of the value on the line C: of 0 at.% in Fig. 1.

The alloy of the second invention should satisfy both the requirement specified in the first invention and a requirement represented by the following inequalities. Points E, F, G, H, and I in Fig. 2 are each a boundary point where two regions cross.

$$5y - 8z \geqq 25 \text{ (here, } z < 5 \text{ at.\%)} \qquad (1)$$

$$5y - 2z \geqq 55 \text{ (5 at.\%} \leqq z < 10 \text{ at.\%)} \qquad (2)$$

$$y \geqq 15 \text{ (10 at.\%} \leqq z < 15 \text{ at.\%)} \qquad (3)$$

$$y + 3z \geqq 60 \text{ (15 at.\%} \leqq z) \qquad (4).$$

wherein y and z represent a value of Al at.% and a value of C at.%, respectively, and the formulae in parentheses represent applicable content regions in respective inequalities.

The lower limit of the C content is more than 0 at.% exclusive of the value on the line C: of 0 at.% in Fig. 2.

The above limitations are provided because when the material is heated from room temperature to a high temperature, if the material brings about transformation, significant expansion or shrinkage occurs at the transformation point. For this reason, the lowest temperature at which the transformation occurs is the upper limit of the service temperature. In the content ranges specified above, the transformation temperature of the material is 800°C or above, indicating that the material can be used as a heat resisting material at a temperature up to 800°C or above and, hence, is suitable for use in high temperature environments of exhaust systems and other systems of vehicles.

The alloy of the third invention should satisfy the requirement specified in the first invention and a requirement represented by the following formula, that is, has a composition falling within the range shown in Fig. 3.

$$C \leqq 12 \text{ at.\%} \quad (5)$$

This limitation is provided because when the C content exceeds 12 at.%, the tensile strength cannot be provided, rendering the strength of the alloy unsatisfactory.

Furthermore, the properties, such as resistance to oxidation, transformation temperature, or the like, are also important for a heat-resisting material besides strength, ductility and fatigue strength at high temperature. Therefore, in the fourth invention, Fe-Al-Si alloy falls within the area formed by connecting points A, J, L, M, B, C and D shown in Fig. 4 and satisfies the formulas hereunder.

$$z_{total} = C + 0.75Si \quad (6)$$

$$0.2 \text{ at.\%} \leqq Si \leqq 10 \text{ at.\%} \quad (7)$$

Namely, the compositions of Al, C and Si are in the range of satisfying the above three conditions. In the range, Si effects changing the transformation temperature, with the result that the heat resistance can be improved by rising the limited temperature of the heat resistance application. More, Si improves the resistance to oxidation, with the result that the heat resistance of the material can be improved. Furthermore, in mechanical properties, Si can enhance graphitization in the composition range of forming a graphite, with the result that castability and workability can be improved. More, Si improves strength and ductility regardless of a graphite formation. However, when the addition of Si exceeds 10 at.% of the above range, elongation deteriorates and brittleness will be caused.

Next, other ingredients according to the invention will be explained below. First, the addition of 0.2 at.% or more of Ti, V, Cr, Ta, W, Nb and Mn as the graphitizer can enhance graphitization in the composition range of forming the graphite, with the result that castability and workability can be improved with increasing strength and ductility of the matrix. More, strength can be improved by dispersing the formed carbides. On the other hand, when the addition of the elements exceeds 2 at.%, the carbides become excessive, with the result that ductility also deteriorates with the decreasing workability due to hardening. Therefore, the elements are limited to the range of from 0.2 to 2.0 at.% in the invention.

More, the addition of 0.2 at.% or more of B and Zr or 0.01 at.% or more of P can enhance graphitization in the composition range of forming the graphite, with the result that castability and workability can be improved with increasing strength and ductility of the matrix. More, strength can be improved by dispersing the formed iron compounds. On the other hand, when the addition of the elements exceeds 2 at.%, the iron compounds become excessive, with the result that ductility also deteriorates with decreasing workability due to hardening. Therefore, B and Zr are limited to the range of from 0.2 to 2.0 at.% and P is limited to the range of from 0.01 to 2.0 at.%.

Furthermore, the addition of 0.2 at.% or more of Ni and Cu can enhance graphitization in the composition range of forming the graphite, with the result that castability and workability with increasing strength and ductility of the matrix. On the other hand, when addition of the elements exceeds 5 at.%, the austenitizing tendency becomes great, with the result that the transformation temperature lowers. Therefore, the elements are limited to the range of from 0.2 to 5.0 at.% in the invention.

Next, the addition of 0.1 at.% or more of Ti, V, Cr, Ta, B, Mo, Sm, Sn, FeB, TaB_2, TiB_2, HfC, TiC, Ag, Ca, Co, Ge, Hf, P, Th, B_4C, NbB_2, Mo_2C, VC, Cr_2N, Fe_3N, Fe_4N, TiN and VN can refine the structure, with the result that strength can be improved with preventing casting defects, such as cracks, segregation or the like. On the other hand, the effect will be saturated if the addition exceeds 2 at.%. More, the addition of 0.1 at.% or more of Ti, Zr, Ce, Er, Gd, Nd, Dy, La, Pr, Y, $BaAl_4$ and Fe_4N softens the structure, with the result that heat fatigue strength can be improved, and further workability can also be improved due to increasing elongation. On the other hand, the effect can be saturated if the addition exceeds 2 at.%. More, the elements of the above may be added as a misch metal.

Furthermore, the addition of Mg enables elongation to increase, and heat fatigue of the material to improve.

The present invention will now be described in more detail with reference to the following examples and comparative examples.

EXAMPLE

Example 1

Alloys having compositions specified in Table 1 were prepared as examples of the first invention and comparative examples. In Table 1, Ex. Nos. 1 to 14 of the present invention are alloys having compositions specified in claim 2 shown in Fig. 1, and Comp. Ex. Nos. 15 to 18 are alloys having compositions outside this composition range.

These alloys were subjected to measurement of the coefficient of linear thermal expansion at 40 to 800°C, and the results are expressed in terms of average coefficient of linear thermal expansion and are also given in Table 1.

Table 1

Classification	No.	Ingredients (at.%)			Average coefficient of linear thermal expansion (40-800°C) ($x10^{-6}$/°C)
		Al	C	Fe	
Ex. of inv.	1	26.3	10.4	Bal.	16.3
	2	25.0	14.7	Bal.	15.8
	3	20.3	0.1	Bal.	14.9
	4	18.9	5.1	Bal.	15.8
	5	20.1	15.6	Bal.	15.3
	6	21.8	22.4	Bal.	15.6
	7	15.2	0.9	Bal.	14.5
	8	14.8	10.9	Bal.	16.9
	9	8.8	0.1	Bal.	14.6
	10	11.0	5.3	Bal.	15.1
	11	9.8	15.0	Bal.	17.0
	12	4.7	1.3	Bal.	14.9
	13	3.8	5.7	Bal.	15.3
	14	4.2	16.1	Bal.	14.3
Comp. Ex.	15	30.5	0	Bal.	20.5
	16	30.1	9.8	Bal.	18.3
	17	34.7	0.9	Bal.	22.7
	18	37.1	11.3	Bal.	23.1

As can be seen from Table 1, for Ex. Nos. 1 to 14 of the present invention, the average coefficients of linear thermal expansion are 14.3 to 17.0 which are better than the average coefficients of linear thermal expansions 18.3 to 23.1 for Comp.Ex. Nos. 15 to 18. Specifically, when the Al content exceeds 28 at.%, the average coefficient of linear thermal expansion becomes excessively large and equal to or larger than that of the austenitic cast iron as a heat resisting material, rendering the material unsuitable for use as a heat resisting material.

When a material to be used at a high temperature has a high coefficient of thermal expansion as in the above material, exposure of the material alternately to a high temperature and a low temperature results in significant expansion/shrinkage of the material. This expansion/shrinkage creates significant strain and stress in adjacent components joined to the member used in a high temperature environment. Further, the material per se also brings about significant strain and stress, because it undergoes constraint by adjacent components, and, in some cases, is broken. For this reason, the lower the coefficient of thermal expansion of the heat resisting material, the better the results.

Example 2

Alloys having compositions specified in Table 2 were prepared as examples of the second invention and comparative examples. In Table 2, Ex. Nos. 19 to 28 of the present invention are alloys having compositions specified in claim (4) shown in Fig. 2, and Comp.Ex. Nos. 29 to 33 are alloys having compositions outside this composition range.

These alloys were subjected to measurement of the transformation temperature, and the results are also given in Table 2.

Table 2

Classification	No.	Ingredients (at.%)			Transformation temp. during cooling (°C)	Transformation temp. during heating (°C)
		Al	C	Fe		
Ex. of inv.	19	8.8	0.1	Bal.	>1000	>1000
	20	9.7	1.6	Bal.	>1000	>1000
	21	14.0	5.1	Bal.	855	887
	22	15.3	9.2	Bal.	838	880
	23	16.1	14.7	Bal.	835	855
	24	15.2	0.9	Bal.	920	940
	25	20.3	0.1	Bal.	>1000	>1000
	26	18.9	5.1	Bal.	>1000	>1000
	27	20.1	15.6	Bal.	>1000	>1000
	28	21.8	22.4	Bal.	>1000	>1000
Comp. Ex.	29	4.7	1.3	Bal.	693	768
	30	11.0	5.3	Bal.	715	775
	31	12.4	8.9	Bal.	748	778
	32	9.8	15.0	Bal.	746	848
	33	4.2	16.1	Bal.	740	768

As can be seen from Table 2, for Ex. Nos. 19 to 28 of the present invention, the transformation temperatures during cooling are 835°C or above which are higher, i.e., better than the transformation temperatures 693 to 748°C for Comp. Ex. Nos. 29 to 33. Specifically, when the composition falls within the range specified in claim (4) shown in Fig. 2, the transformation temperature is above 800°C which exceeds that of high-silicon heat-resisting cast iron. Further, as demonstrated in Example 1, the coefficient of thermal expansion is low, i.e., excellent, indicating that the materials of the present invention have good properties as a heat resisting material.

Example 3

Alloys having compositions specified in Table 3 were prepared as examples of the third invention and comparative examples. In Table 3, Ex. Nos. 34 to 41 of the present invention are alloys having compositions specified in claim (6) shown in Fig. 3, and Comp. Ex. Nos. 42 to 44 are alloys having compositions outside this composition range.

These alloys were subjected to measurement of the tensile strength at room temperature, and the results are also given in Table 3.

Table 3

Classification	No.	Ingredients (at.%)			Tensile strength (MPa)
		Al	C	Fe	
Ex. of inv.	34	3.8	5.7	Bal.	959
	35	4.1	11.3	Bal.	652
	36	11.0	5.3	Bal.	854
	37	10.9	10.7	Bal.	494
	38	14.0	5.1	Bal.	455
	39	14.8	10.9	Bal.	636
	40	18.9	5.1	Bal.	489
	41	20.3	0.1	Bal.	501
Comp. Ex.	42	4.2	16.1	Bal.	140
	43	9.8	15.0	Bal.	195
	44	16.1	14.7	Bal.	96

As can be seen from Table 3, for Ex. Nos. 34 to 41 of the present invention, the tensile strengths at room temperature are 489 to 959 MPa which are better than the tensile strengths at room temperature 96 to 195 MPa for Comp.Ex. Nos. 42 to 44. Specifically, when the C content exceeds 12 at.%, the tensile strength at room temperature is lowered. For heat resisting materials, the tensile strength at a high temperature is about 1/3 of that at room temperature. This value is proportional to that at room temperature. Further, as demonstrated in Example 1, the coefficient of thermal expansion is low, i.e., excellent. These facts indicate that the materials of the present invention have good properties as a heat resisting material.

Example 4

Alloys having compositions specified in Table 4 were prepared as examples of the fourth invention and comparative examples. In Table 4, Ex. Nos. 45 to 50 of the present invention are alloys having compositions specified in claim 6 shown in Fig. 4, and Comp. Ex. Nos. 51 and 52 are alloys having compositions outside this composition range.

These alloys were subjected to measurement of the transformation temperature during cooling and heating, and the results are also given in Table 4.

Table 4

Classification	No.	Ingredients (at.%)					Transformation temp. during cooling (°C)	Transformation temp. during heating (°C)
		Al	z_{total}	C	Si	Fe		
Ex. of inv.	45	8.1	4.2	0.4	5.0	Bal.	810	858
	46	10.0	6.9	4.0	3.8	Bal.	808	837
	47	7.1	12.4	7.3	6.8	Bal.	823	848
	48	20.1	5.1	4.0	1.5	Bal.	911	948
	49	22.3	14.0	10.1	5.2	Bal.	>1000	>1000
	50	20.2	19.9	14.9	6.7	Bal.	>1000	>1000
Comp. Ex.	51	4.0	5.2	3.9	1.7	Bal.	730	820
	52	3.1	10.0	8.4	2.1	Bal.	708	785

As can be seen from Table 4, for Ex. Nos. 45 to 50 of the present invention, the transformation temperatures are 808°C or above during cooling and 837°C or above during heating, respectively, which are higher, i.e., better than the transformation temperatures of 730°C or under during cooling and 820°C or under during heating for Comp. Ex. Nos. 51 and 52. Therefore, as mentioned above, the limited temperature of the heat resistance application rises, with the result that the heat resistance can be improved and the graphitization can be enhanced.

Example 5

Next, the examples of improving the properties by adding other ingredients according to the present invention will be explained below.

First, as the examples of the graphitizer, alloys having compositions specified in Table 5 were prepared as examples of adding the graphitizer and comparative examples. These alloys were subjected to measurement of graphite amount after casting, and the results are also given in Table 5.

Table 5

Classification	Ingredients (at.%)					Graphite amount (%)
	Al	C	Added element, amount		Fe	
Without addition	18.9	15.2	No-addition		Bal.	2.6
With addition	16.8	15.2	Ti	0.3	Bal.	3.5
	21.5	14.8	V	0.5	Bal.	5.8
	18.1	14.6	Cr	0.5	Bal.	4.8
	17.5	15.4	Ta	0.4	Bal.	7.5
	19.0	13.9	W	0.2	Bal.	4.0
	20.1	14.5	Nb	0.5	Bal.	3.4
	18.7	14.1	Mn	0.4	Bal.	3.2
	18.5	14.2	B	0.6	Bal.	3.6
	18.4	14.9	Zr	0.5	Bal.	3.1
	19.1	15.6	Ni	0.8	Bal.	4.6
	20.3	15.1	Cu	0.8	Bal.	3.1
	19.5	14.6	P	0.5	Bal.	6.0

As can be seen from Table 5, although the graphite amount of adding the graphitizer in the present invention is 3.1 to 7.5%, the Comp. Ex. without adding the graphitizer has 2.6% of the graphite amount, i.e., the effect of the graphitizer according to the present invention is remarkably exhibited in the scope of the present invention.

Next, as examples adding the element for refining, the examples adding TiB_2 are shown in Figs. 5(a) to 5(c). Figs. 5(a) to 5(c) show the metallic structure photographs of three magnifications after casting of Fe - 10% at.% Al - 2 at.% C alloy without addition, of Fe - 10 at.% Al - 2 at.% C alloy adding 0.8 at.% TiB_2 and of Fe - 10 at.% Al - 2 at.% alloy adding 1.9 at.% TiB_2, respectively. From these photographs, the above effect of refining can remarkably exhibited in the scope of the present invention.

Furthermore, as examples of ingredients for improving softening and ductility, alloys having compositions specified in Table 6 were prepared with addition and without addition of the element. These alloys were subjected to measurement of hardness after casting, and the results are also given in Table 6.

Table 6

Classification	Ingredients (at.%)					Hardness
	Al	C	Added element, amount		Fe	Hv (20 kg)
Without addition	10.1	5.0	No-addition		Bal.	334
With addition	9.8	4.9	Ti	1.6	Bal.	302
	9.7	5.1	Zr	1.5	Bal.	306
	10.2	5.2	Ce	1.3	Bal.	244
	9.7	4.9	Er	1.5	Bal.	253
	9.6	5.3	Gd	1.6	Bal.	231
	9.8	5.2	Nd	1.4	Bal.	288
	10.1	5.1	Dy	1.7	Bal.	274
	9.9	5.0	misch metal	1.3	Bal.	221
	10.3	5.3	La	1.7	Bal.	282
	9.8	4.9	Pr	1.6	Bal.	231
	9.5	5.1	Y	1.7	Bal.	301
	9.6	5.2	$BaAl_4$	1.3	Bal.	325
	9.7	5.3	Fe_4N	1.4	Bal.	299

As can be seen from Table 6, for alloys with addition of the present invention, the hardness values are 221 to 306 of Vickers Hardness, i.e., better than the hardness value 334 of Vickers Hardness without addition. Namely, the effect of improving softening and ductility can remarkably exhibited in the scope of the present invention.

Furthermore, as examples of adding Mg, alloys having compositions specified in Table 7 were prepared with addition and without addition of Mg. These alloys were subjected to measurement of tensile strength and elongation after casting, and the results are also given in Table 7.

Table 7

Classification	Ingredients (at.%)					Tensile strength (MPa)	Elongation (%)
	Al	C	Si	Mg	Fe		
Without addition	11.0	5.3	-	-	Bal.	854	2.7
	10.1	15.3	-	-	Bal.	304	0.8
	4.2	16.1	-	-	Bal.	140	0.4
With addition	11.3	5.1	2.1	0.06	Bal.	976	4.2
	9.7	14.9	6.5	0.04	Bal.	669	3.9
	4.0	15.7	4.7	0.06	Bal.	365	8.1

As can be seen from Table 7, for alloys with addition of the present invention, the elongation values are 3.9 to 8.1%, i.e., better than the elongation values 0.4 to 2.7% without addition. Namely, the effect of improving elongation can remarkably exhibited by adding Mg to the alloys according to the present invention.

The materials of the present invention, despite the fact that they are mainly ternary alloys consisting of Fe, Al, and C without use an amount of expensive alloying elements, such as Cr and Ni, have excellent high-temperature heat resisting properties, i.e., low coefficient of linear thermal expansion and enhanced transformation temperature and excellent tensile strength, and, hence, can be applied to members to be used at higher temperatures. In particular, the materials of the present invention have a transformation temperature of 800°C or above, rendering the materials of the present invention suitable for use in high temperature environments in an exhaust system and other systems of vehicles.

Claims

1. A high heat-resisting iron-base alloy characterized in essentially consisting of a composition, in terms of atomic %, which is represented by the general formula: $Fe_xAl_yC_z$, wherein y and z are $1\% \leqq y(at.\%) \leqq 28\%$ and $0\% < z(at.\%) \leqq 24\%$, respectively, with x being the remainder.

2. A high heat-resisting iron-base alloy according to claim 1, wherein y and z fall within the area formed by connecting points A(1, 24), B(1, 0), C(28, 0) and D(28, 24) shown in Fig. 1, provided that values on line C: of 0% are excluded.

3. A high heat-resisting iron-base alloy according to claim 1, wherein y and z further satisfy the inequalities (1) to (4) hereunder;

$$5y - 8z \geqq 25 \text{ (here, } z < 5 \text{ at.\%)} \quad (1)$$

$$5y - 2z \geqq 55 \text{ (5 at.\%} \leqq z < 10 \text{ at.\%)} \quad (2)$$

$$y \geqq 15 \text{ (10 at.\%} \leqq z < 15 \text{ at.\%)} \quad (3)$$

$$y + 3z \geqq 60 \text{ (15 at.\%} \leqq z) \quad (4).$$

4. A high-resisting iron-base alloy according to claim 1, wherein y and z fall within the area formed by connecting points A(1, 24), E(1, 19), F(15, 15), G(15, 10), H(13, 5), I(5, 0), C(28, 0) and D(28, 24) shown in Fig. 2, provided that values on line C: of 0% are excluded.

5. A high heat-resisting iron-base alloy according to claim 1, wherein y and z further satisfy the inequality (5) hereunder;

$$z \leqq 12 \text{ at.\%} \quad (5).$$

6. A high heat-resisting iron-base alloy according to claim 1, wherein y and z fall within the area formed by connecting points J(1, 12) B(1, 0), C(28, 0) and K(28, 12) shown in Fig. 3, provided that values on line C: of 0% are excluded.

7. A high heat-resisting iron-base alloy characterized in essentially consisting of a composition, in terms of atomic %, which is represented by the general formula: $Fe_xAl_vSi_{z1}C_{z2}$, wherein y, z_1 and z_2 fall within the area formed by connecting points A(1, 24), J(1, 12), L(8, 10), M(7, 5), B(1, 0), C(28, 0) and D(28, 24) shown in Fig. 4, in which $z_{total} = z_2 + 0.75z_1$, and $0.2 \text{ at.\%} \leqq z_1 \leqq 10 \text{ at.\%}$.

8. A high heat-resisting iron-base alloy according to any one of claims 1 to 7 further comprising a graphitizer.

9. A high heat-resisting iron-base alloy according to claim 8 further comprising 0.2 to 2.0 at.% of at least one element selected from the group of Ti, V, Cr, Ta, W, Nb and Mn as the graphitizer.

10. A high heat-resisting iron-base alloy according to claim 8 further comprising 0.2 to 2.0 at.% of one or both of B and Zr as the graphitizer.

11. A high heat-resisting iron-base alloy according to claim 8 further comprising 0.01 to 0.2 at.% of P as the graphitizer.

12. A high heat-resisting iron-base alloy according to claim 8 further comprising 0.2 to 5.0 at.% of one or both of Ni and Cu as the graphitizer.

13. A high heat-resisting iron-base alloy according to any one of claims 1 to 12 further comprising an element or a compound for refining.

14. A high heat-resisting iron-base alloy according to claim 13 further comprising 0.1 at.% or more of at least one selected from the group of Ti, V, Cr, Ta, B, Mo, Sm, Sn, FeB, TaB_2, TiB_2, HfC, TiC, Ag, Ca, Co, Ge, Hf, P, Yb, B_4C, NbB_2, Mo_2C, VC, Cr_2N, Fe_3N, Fe_4N, TiN and VN as the element or the compound for refining.

15. A high heat-resisting iron-base alloy according to any one of claims 1 to 14 further comprising an element or a compound for improving ductility.

16. A high heat-resisting iron-base alloy according to claim 15 further comprising 0.1 at.% or more of at least one selected from the group of Ce, Er, Gd, Nd, Dy, La, Pr, Y, $BaAl_4$ and Fe_4N as the element or the compound for improving ductility.

Fig.1

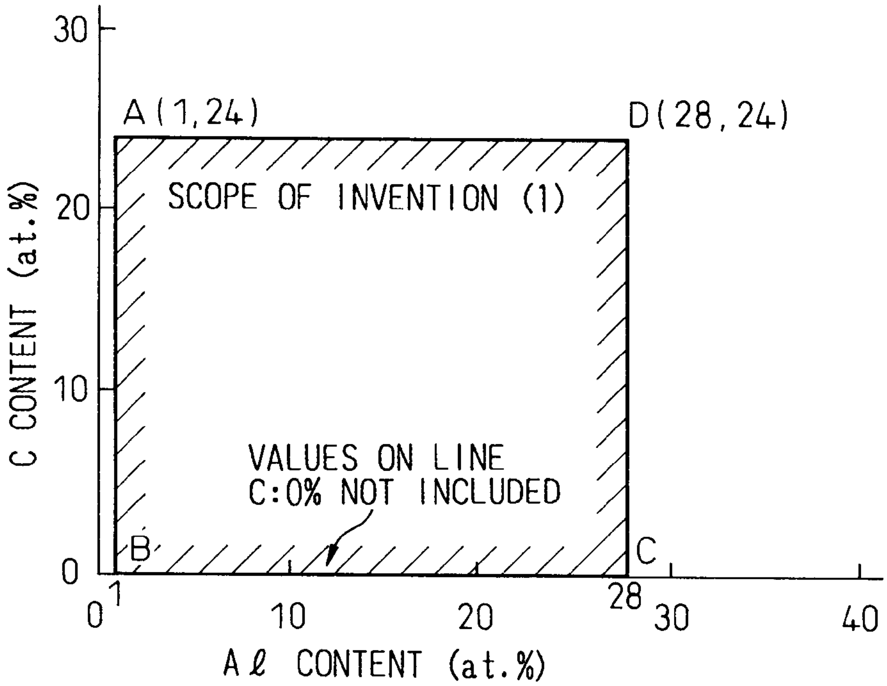

30
20
10
0
A (1,24)
D (28,24)
SCOPE OF INVENTION (1)
VALUES ON LINE
C:0% NOT INCLUDED
B
C
0
1
10
20
28
30
40
C CONTENT (at.%)
Aℓ CONTENT (at.%)

Fig.2

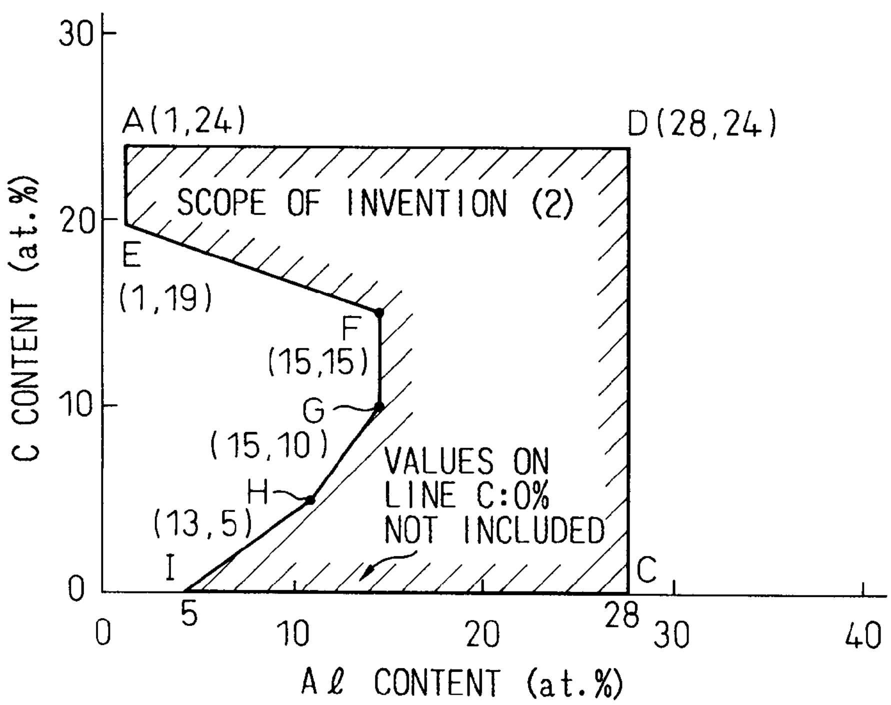

30
20
10
0
A(1,24)
D(28,24)
SCOPE OF INVENTION (2)
E
(1,19)
F
(15,15)
G
(15,10)
H
(13,5)
I
VALUES ON
LINE C:0%
NOT INCLUDED
C
0
5
10
20
28
30
40
C CONTENT (at.%)
Aℓ CONTENT (at.%)

Fig.3

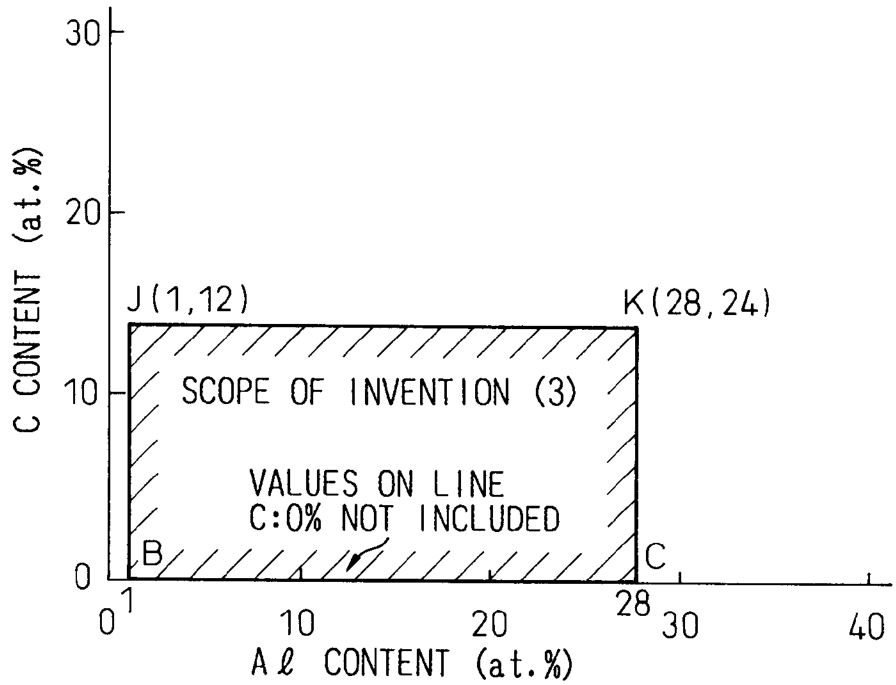

30
20
10
0
C CONTENT (at.%)
J(1,12)
K(28,24)
SCOPE OF INVENTION (3)
VALUES ON LINE
C:0% NOT INCLUDED
B
C
0
1
10
20
28
30
40
Aℓ CONTENT (at.%)

Fig.4

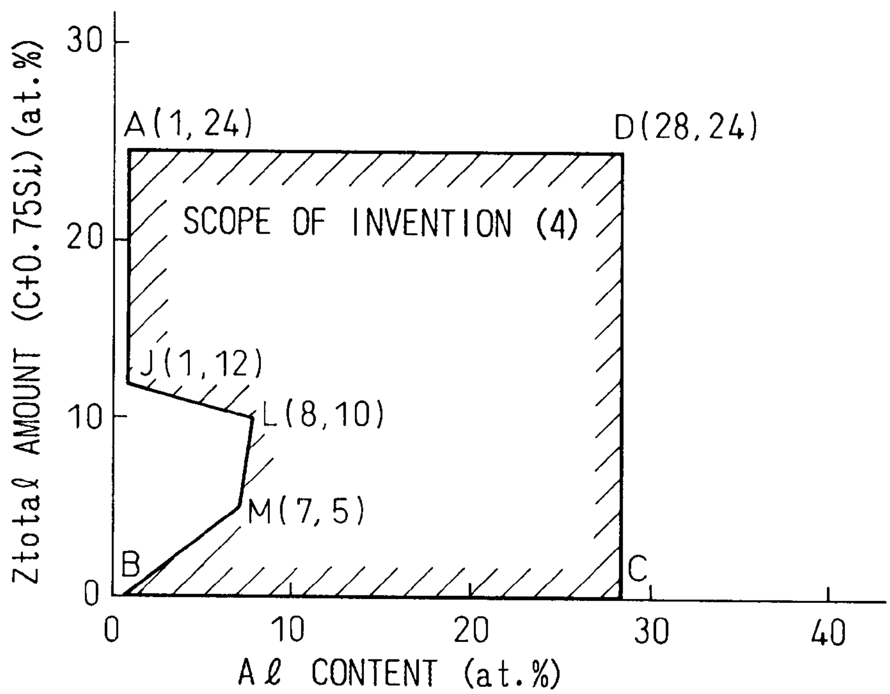
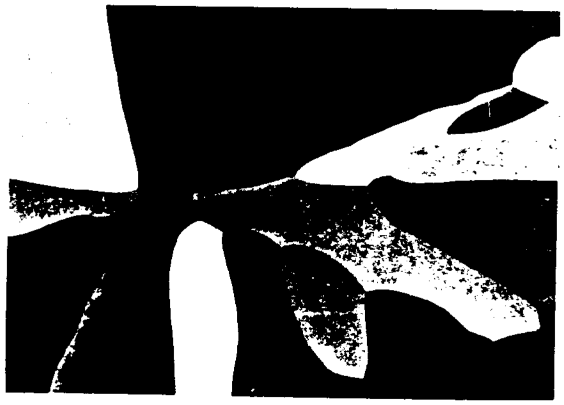
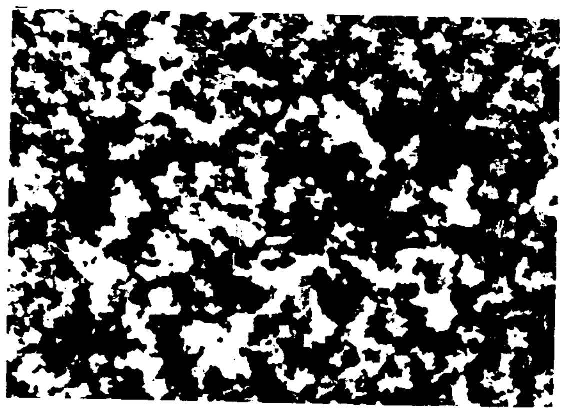

30
20
10
0
Ztotalℓ AMOUNT (C+0.75Si) (at.%)
A(1,24)
D(28,24)
SCOPE OF INVENTION (4)
J(1,12)
L(8,10)
M(7,5)
B
C
0
10
20
30
40
Aℓ CONTENT (at.%)

Fig.5(a)



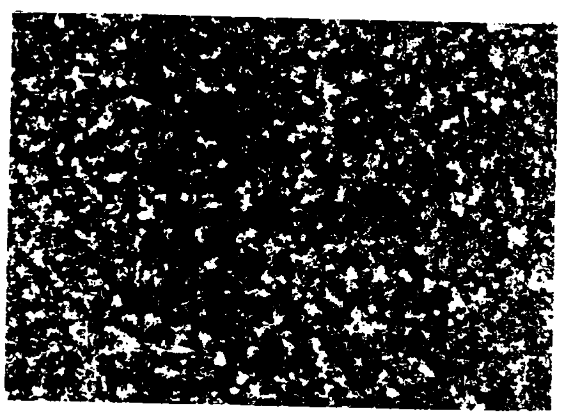
(×3)

Fig.5(b)



(×3)

Fig.5(c)



(×3)

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 30 5233

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	US-A-4 501 612 (STEFANESCU DORU M ET AL) 26 February 1985 * claim 1 *	1-7	C22C37/10
X	GB-A-2 186 886 (NIPPON STEEL CORP) 26 August 1987 * claims 1,5,10 *	1-7	
X	PATENT ABSTRACTS OF JAPAN vol. 012 no. 117 (C-487) ,13 April 1988 & JP-A-62 240746 (YAMAHA MOTOR CO LTD) 21 October 1987, * abstract *	1-7	
X	PATENT ABSTRACTS OF JAPAN vol. 012 no. 353 (C-530) ,21 September 1988 & JP-A-63 109141 (NISSAN MOTOR CO LTD) 13 May 1988, * abstract *	1-7	
X	PATENT ABSTRACTS OF JAPAN vol. 006 no. 006 (E-089) ,14 January 1982 & JP-A-56 129303 (TDK CORP) 9 October 1981, * abstract *	1-7	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C22C
A	PATENT ABSTRACTS OF JAPAN vol. 007 no. 053 (C-154) ,3 March 1983 & JP-A-57 203750 (NIPPON DENKI KK) 14 December 1982, * abstract *	1	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	31 October 1995	Gregg, N

CATEGORY OF CITED DOCUMENTS

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

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