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

(11) **EP 1 205 568 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
01.12.2004 Bulletin 2004/49

(21) Application number: **00929875.3**

(22) Date of filing: **26.05.2000**

(51) Int Cl.[7]: **C22C 27/06**

(86) International application number:
PCT/JP2000/003399

(87) International publication number:
WO 2000/073523 (07.12.2000 Gazette 2000/49)

(54) Cr-BASE ALLOY EXCELLENT IN BALANCE BETWEEN STRENGTH AND DUCTILITY AT HIGH TEMPERATURE

AUF CHROM BASIERENDE LEGIERUNG MIT AUSGEZEICHNETEM GLEICHGEWICHT ZWISCHEN FESTIGKEIT UND DUKTILITÄT BEI HOHEN TEMPERATUREN

ALLIAGE A BASE DE CHROME DOTE D'UN EXCELLENT EQUILIBRE RESISTANCE-DUCTILITE A HAUTE TEMPERATURE

(84) Designated Contracting States:
DE FR GB

(30) Priority: **27.05.1999 JP 14832699**

(43) Date of publication of application:
15.05.2002 Bulletin 2002/20

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Description

TECHNICAL FIELD

[0001] This invention relates to a Cr-based alloy having an excellent strength-ductility balance at high temperatures (not lower than 1000°C, particularly super-high temperature zone of not lower than 1050°C).

BACKGROUND ART

[0002] With the advance of techniques in recent industrial and manufacturing fields and the rise of interest in environmental problem, it is strongly demanded to develop metallic materials having high strength and ductility at higher temperatures, particularly a high temperature zone of not lower than 1000°C.

[0003] EP-A1-0 597 129 discloses Fe-Cr alloys having up to 60% wt Cr with improved ductility by reducing the total content of interstitial elements C, N, O, P, and S below 100 ppm.

[0004] Incidentally, high-temperature materials used from the old time were mainly Ni-based, Cr-based and Co-based alloys. For example, JP-B-64-7145 proposes Ni-based alloy comprising Cr: 20-35 wt%, Si: 1-8 wt% and C: 1.7-3.5 wt% and forming M_7C_3 type carbide, and also JP-A-55-154542 proposes Ni-Co-Cr based alloy comprising Ni: 20-47 wt%, Co: 6-35 wt%, Cr: 18-36 wt%, C: 0.6-2.5 wt% and Si: 0.5-2.5 wt%. However, all of these alloys could be practically used up to only a temperature of about 500°C. And also, these alloys containing a greater amount of Ni or Co have many problems that the cost of the material itself is very expensive and the thermal expansion coefficient is high.

[0005] A Cr-based alloy is hopeful as a high-temperature material being cheaper than Ni- or Co-based alloy and small in the thermal expansion coefficient. For example, JP-A-11-80902 proposes a high-Cr alloy containing C: 0.5-1.5 wt%, Si: 1.0-4.0 wt%, Mn: 0.5-2.0 wt% and Cr: 35-60 wt% and enhancing a resistance to erosion and corrosion at a higher temperature. However, even in this high-Cr alloy, it is difficult to obtain a sufficient strength at a high temperature zone, particularly above 1000°C. In order to further increase the strength of such a Cr-based alloy, it is required to more increase the Cr amount. In the conventional technique, however, when the Cr amount is not less than 60 mass%, the ductility is substantially lost, so that there is a problem that the working after the production is impossible. Therefore, the alloy containing Cr of not less than 60 mass% has been not yet put into practical use.

[0006] As mentioned above, practical materials having a sufficient strength at the high temperature and a good workability (ductility) is not existent in spite of a situation that it is more increased to demand materials durable to use under a super-high temperature environment.

[0007] It is, therefore, an object of the invention to solve the above problems of the conventional technique and to provide Cr-based alloys having an excellent strength-ductility balance, which has never been attained in the conventional alloy, at a high temperature above 1000°C, particularly a high temperature above 1050°C.

DISCLOSURE OF INVENTION

[0008] The inventors have made various studies in order to solve the above problems by using the Cr-based alloy useful from economical reason and thermal expansion coefficient. As a result, it has been found that even in the Cr-based alloy containing Cr of not less than 60 mass%, the ductility can be provided and the high-temperature strength and ductility can be established by controlling contents of C+N, S and O in the alloy and an amount of an oxide to not more than limiting amounts and the invention has been accomplished.

[0009] According to the present invention there is provided a Cr-based alloy having an excellent strength-ductility balance at higher temperatures, comprising Cr, C, N, S and O with the remainder being Fe and inevitable impurities wherein the Cr content is greater than 60 mass %, the sum of the C and N contents is in the range 0.1-10 mass ppm, the S content is in the range 0.1-10 mass ppm, the total O content is in the range 5-50 mass ppm, and the content of O as an oxide is in the range 3-30 mass ppm.

[0010] It is particularly preferred for the Cr content to be not less than 65 mass %.

[0011] Embodiments of the invention result in alloys having a strength-ductility balance of RA x TS ≥ 10000 (% . MPa) at higher than 1000°C and even at 1050°C-1200°C.

BRIEF DESCRIPTION OF DRAWING

[0012]

Fig. 1 is a graph showing the relationship between strength-ductility balance at 1100°C and C+N amount.

BEST MODE FOR CARRYING OUT THE INVENTION

[0013] Firstly, there is described an experiment arriving at the invention.

[0014] Various Cr-based alloys containing 65 mass % of Cr were produced by changing purities of starting materials and melting conditions and shaped into rod-shaped specimens of 25mm by hot forging. In this case, hot forging → working → reheating → hot forging were repeated with respect to alloys hardly working into a rod because of poor workability. These rod-shaped specimens were heated to 1250° and water-cooled, from which round specimens of 6.5 mm in diameter and 120mm in length were cut out. The strength (tensile strength) and ductility (reduction of cross section) at 1100°C were measured using these round specimens by means of a high-temperature tensile testing machine of direct current system (Greeble testing machine).

[0015] In Fig. 1 is shown the influence of C+N amount upon strength-ductility balance (product of reduction of cross section RA by tensile strength TS) at a high temperature. From Fig. 1, it can be understood that it is required to decrease the C+N amount and also control S amount and O amount in order to provide RA × TS ≧ 10000 (%·MPa) as a good region of strength-ductility balance at a high temperature zone. The invention is accomplished based on such a knowledge.

[0016] The reason why the components according to the invention are restricted to the above ranges is described below.

Cr: not less than 60 mass%

[0017] Cr is an element required for ensuring the strength at the high temperature. When the amount is less than 60 mass%, it is difficult to ensure the strength above 1000°C, so that it is required to be not less than 60 mass%. Moreover, it is favorable to be not less than 65 mass% in order to develop sufficient properties. Also, the upper limit of Cr amount is not particularly restricted, but 99.99 mass% is critical from a viewpoint of production by melting.

·C+N: not more than 20 mass ppm

[0018] C and N form carbonitride of Cr below 1000°C to bring about brittleness of Cr-based alloy and degradation of corrosion resistance. Also, C and N are existent in a solid solution state at a high temperature zone above 1000°C to lower the ductility. In order hot to bring about the degradation of these properties, C+N are required to be not more than 20 mass ppm. Moreover, in order to more lessen the degradation of the ductility, C+N are favorable to be not more than 10 mass ppm. Furthermore, the lower limit is restricted, to 0.1 mass ppm considering the melt production time in industry.

·S: not more than 20 mass ppm

[0019] S exists in form of a sulfide with a slight amount of a metallic element such as Ti, Cu, Mn or the like slightly included in the Cr-based alloy, or segregates in a grain boundary at a solid solution state. In any case, it brings about the degradation of the ductility. Such a degradation of the ductility becomes remarkable when the S amount exceeds 20 mass ppm, so that the upper limit is 20 mass ppm. Moreover, in order to more lessen the degradation of the ductility, it is desirable to control the S amount to not more than 10 mass ppm. Also, the lower limit of the S amount is restricted, to 0.1 mass ppm considering the melt producing cost.

·O (total O): not more than 100 mass ppm, O as an oxide: not more than 50 mass ppm

[0020] O forms an oxide with a slight amount of a metallic element such as Al, Si or the like slightly included in the Cr-based alloy to bring about the degradation of the ductility. In order to avoid such a bad influence, it is necessary that the O amount (total O amount) is restricted to not more than 100 mass ppm and the O amount existing as an oxide is controlled to not more than 50 mass ppm. Moreover, in order to maintain the high ductility, it is favorable that the O amount is not more than 50 mass ppm and the O amount as an oxide is not more than 30 mass ppm. The lower limits of the O amount and the O amount as an oxide are restricted, to 5 mass ppm and 3 mass ppm, respectively, considering the melt producing cost.

[0021] In addition to the aforementioned elements, there are Fe and inevitable impurities. Moreover, the reason why the remaining element is Fe is due to the fact that Cr-Fe alloy is most advantageous from a viewpoint of the ductility and the cost.

[0022] The alloy according to the invention has excellent strength and ductility at a high temperature region above 2000°C. Such an alloy can be particularly produced according to usual manner except that starting materials having a higher purity are used and melting conditions are paid attention to. In this case, it is desirable that chromium of not less than 99.9 mass% is used as the starting material and the melting conditions are the use of skull melting process resulting in less incorporation of impurities from the crucible and a vacuum degree of 10^{-5} Torr.

EXAMPLE

[0023] Various Cr-based alloys having a chemical composition as shown in Table 1 are produced by melting. In the melt production, a high purity chromium (purity: 99.95 mass%) and a super-high purity electrolytic iron (purity: 99.998 mass%) are used and a skull melting process using a water-cooled copper crucible is adopted. The resulting ingot is hot forged at 956-1200°C (forging is carried out by repeating hot forging → working → reheating → hot forging at a temperature region more giving a ductility) to form a rod-shaped specimen of 25 mm.

[0024] The rod-shaped specimen is heated to 1250°C and water-cooled, from which is cut out a round specimen of 6.5 mm in diameter and 120 mm in length. The ductility (reduction of cross section) at a high temperature is measured with respect to such a specimen by means of a high-temperature tensile testing machine of direct current system (Greeble testing machine). For comparison, the same test is carried out with respect to 54Ni-18Cr-3Mo alloy (Inconel 718) as a commercial heat-resistant material.

(Table 1)

Alloy	Cr /mass%	C+N /mass ppm	S /mass ppm	O /mass ppm	O as Oxide /mass ppm	Remarks
A	50	0.9	0.6	9	4	Comparative Example
B	50	31	18	17	9	Comparative Example
C	65	1.2	0.9	5	3	Example
D	65	7.5	8.1	20	13	Example
E	65	8.2	7.7	80	40	Example
F	65	25	9.3	80	30	Comparative Example
G	65	9.1	32.2	60	25	Comparative Example
H	65	8.2	7.6	110	70	Comparative Example
I	70	9.1	9.5	31	26	Example
J	80	2.6	3.8	31	22	Example
K	90	5.4	6.2	32	22	Example
L	≧ 99.9	9.8	7.5	44	29	Example
M	54Ni-18Cr-3.OMo-18.5Fe		-	-	-	Conventional Example

[0025] The measured results of high-temperature tensile test are shown in Table 2. In the alloys A and B containing less than 60 mass% of Cr, the strength at the high temperature lowers. Also, 54Ni-18Cr-3Mo alloy used as a heat-resistant material from the old times violently lowers the ductility above 1000°C and renders RA at 1200°C into 0%.

[0026] On the contrary, the invention alloys indicate RA × TS ≧ 10000 (%·MPa) showing a strength-ductility balance at a high temperature above 1000°C and have a very excellent strength-ductility balance.

(Table 2)

Alloy	RA(%)					TS(MPa)					RA×TS (%·MPa)					Remarks
	900°C	1000°C	1050°C	1100°C	1200°C	900°C	1000°C	1050°C	1100°C	1200°C	900°C	1000°C	1050°C	1100°C	1200°C	
A	82	78	81	89	92	195	160	121	100	75	15990	12480	9801	8900	6900	Comparative Example
B	47	62	65	68	72	235	150	120	90	70	11045	9300	7800	6120	5040	Comparative Example
C	79	87	93	98	100	339	243	210	176	131	26781	21141	19379	17248	13100	Example
D	72	85	89	93	95	325	241	205	168	124	23400	20485	18201	15624	11780	Example
E	65	80	84	87	91	291	233	197	160	115	18915	18640	16408	13920	10465	Example
F	58	81	61	62	79	280	210	151	148	112	16240	12810	8211	9178	8848	Comparative Example
G	45	53	54	59	67	276	228	156	152	107	12420	12084	8424	8968	7169	Comparative Example
H	54	62	63	68	72	271	223	150	142	99	14634	13826	9450	9656	7128	Comparative Example
I	72	84	69	93	98	335	242	210	177	128	24120	20328	18541	16461	12544	Example
J	66	82	86	90	96	332	240	210	180	142	21912	19680	18060	16200	13632	Example
K	68	80	85	89	96	331	236	209	182	146	22508	18880	17661	16198	14016	Example
L	69	80	84	87	95	331	238	212	185	150	22839	19040	17660	16095	14260	Example
M	84	86	21	8	0	462	315	264	212	49	38808	27090	5534	1696	0	Conventional Example

INDUSTRIAL APPLICABILITY

[0027] As mentioned above, according to the invention, there can be provided Cr-based alloys having an excellent strength-ductility balance at a higher temperature above 1000°C, particularly above 1050°C. Therefore, the invention conduces in various industry fields requiring a high-temperature material and largely contributes to the improvement of earth environment.

Claims

1. A Cr-based alloy having an excellent strength-ductility balance at higher temperatures, comprising Cr, C, N, S and O with the remainder being Fe and inevitable impurities wherein the Cr content is greater than 60 mass %, the sum of the C and N contents is in the range 0.1-10 mass ppm, the S content is in the range 0.1-10 mass ppm, the total O content is in the range.5-50 mass ppm, and the content of O as an oxide is in the range 3-30 mass ppm.

2. A Cr-based alloy as claimed in claim 1 wherein the Cr content is not less than 65 mass %.

Patentansprüche

1. Legierung auf Cr-Basis mit einem hervorragenden Gleichgewicht zwischen Festigkeit und Verformbarkeit bei höheren Temperaturen, umfassend Cr, C, N, S und O, wobei der Rest Fe und unvermeidbare Verunreinigungen ist, der Cr-Gehalt größer als 60 Masseprozent ist, die Summe des Gehalts an C und N im Bereich von 0,1 bis 10 Masse-ppm ist, der S-Gehalt im Bereich von 0,1 bis 10 Masse-ppm ist, der gesamte O-Gehalt im Bereich von 5 bis 50 Masse-ppm ist, und der Gehalt an O als Oxid im Bereich von 3 bis 30 Masse-ppm ist.

2. Legierung auf Cr-Basis nach Anspruch 1, wobei der Cr-Gehalt nicht kleiner als 65 Masseprozent ist.

Revendications

1. Alliage à base de chrome ayant un excellent équilibre résistance mécanique/ductilité à haute température, contenant Cr, C, N, S et O, le reste étant constitué de Fe et d'inévitables impureté, la teneur en Cr étant supérieure à 60 % de la masse, la somme des teneurs en C et N étant de 0,1 à 10 ppm de masse, la teneur en S étant de 0,1 à 10 ppm de masse, la teneur totale en O étant de 5 à 50 ppm de masse et la teneur en O sous la forme d'oxyde étant de 3 à 30 ppm de masse.

2. Alliage à base de chrome selon la revendication 1, dans lequel la teneur en Cr n'est pas inférieure à 65 % de la masse.

Fig.1

	Cr mass %	S mass ppm	O mass ppm	O as Oxide mass ppm
○	65	1.0～5.0	10～ 20	12～ 18
△	65	35～ 40	35～ 45	30～ 40
□	65	5～ 10	120～150	80～100