

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11)

EP 1 205 568 A1

(12)

**EUROPEAN PATENT APPLICATION**  
published in accordance with Art. 158(3) EPC

(43) Date of publication:

15.05.2002 Bulletin 2002/20

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

(21) Application number: **00929875.3**

(86) International application number:  
**PCT/JP00/03399**

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

(87) International publication number:  
**WO 00/73523 (07.12.2000 Gazette 2000/49)**

(84) Designated Contracting States:  
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE**  
Designated Extension States:  
**AL LT LV MK RO SI**

(72) Inventor: **ABIKO, Kenji**  
**Sendai-shi, Miyagi 981-3203 (JP)**

(74) Representative: **Stebbing, Timothy Charles**  
**Haseltine Lake & Co.,**  
**Imperial House,**  
**15-19 Kingsway**  
**London WC2B 6UD (GB)**

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

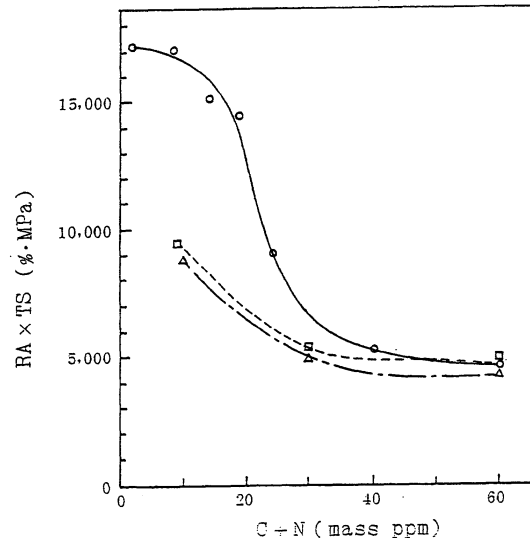
(71) Applicant: **Japan Science and Technology  
Corporation**  
**Kawaguchi-shi, Saitama 332-0012 (JP)**

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

(57) A strength-ductility balance at a high temperature above 1000°C, particularly a high temperature above 1050°C is improved by rendering a chemical composition of Cr-based alloy into Cr: not less than 60 mass%, C+N: not more than 20 mass ppm, S: not more than 20 mass ppm, O: not more than 100 mass ppm, O as an oxide: not more than 50 mass ppm, and the remainder being Fe and inevitable impurities.

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



EP 1 205 568 A1

**Description**

## TECHNICAL FIELD

5 **[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

10 **[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.

15 **[0003]** Incidentally, high-temperature materials used from the old time were mainly Ni-based, Cr-based and Co-based alloys. For example, JP-A-55-154542 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.

20 **[0004]** 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%,  
25 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.

**[0005]** 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.

30 **[0006]** 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

35 **[0007]** 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  
40 more than limiting amounts and the invention has been accomplished.

**[0008]** The invention lies in a Cr-based alloy having an excellent strength-ductility balance at higher temperatures, comprising Cr: not less than 60 mass%, C+N: not more than 20 mass ppm, S: not more than 20 mass ppm, O: not more than 100 mass ppm, O as an oxide: not more than 50 mass ppm, and the remainder being Fe and inevitable impurities.

45

## BRIEF DESCRIPTION OF DRAWING

**[0009]** Fig. 1 is a graph showing a relation between strength-ductility balance at 1100°C and C+N amount.

## 50 BEST MODE FOR CARRYING OUT THE INVENTION

**[0010]** Firstly, there is described an experiment arriving at the invention.

**[0011]** Various Cr-based alloys containing 65 mass% of Cr are produced by changing purities of starting materials and melting conditions and shaped into rod-shaped specimens of 25 mm by hot forging. In this case, hot forging →  
55 working → reheating → hot forging are repeated with respect to alloys hardly working into a rod because of poor workability. These rod-shaped specimens are heated to 1250°C and water-cooled, from which round specimens of 6.5 mm in diameter and 120 mm in length are cut out. The strength (tensile strength) and ductility (reduction of cross section) at 1100°C are measured by using these round specimens by means of a high-temperature tensile testing

machine of direct current system (Greeble testing machine).

**[0012]** In Fig. 1 is shown an 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 is understood that it is required to only decrease the C+N amount but also control S amount and O amount in order to provide  $RA \times TS \geq 10000$  (%-MPa) as a good region of strength-ductility balance at a high temperature zone. The invention is accomplished based on such a knowledge.

**[0013]** The reason why the components according to the invention are restricted to the above ranges is described below.

- Cr: not less than 60 mass%

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. And 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

C and N form carbonitride of Cr below 1000°C to bring about brittleness of Cr-based alloy and degradation of corrosion resistance. And also, C and N are existent at a solid solution state at a high temperature zone above 1000°C to lower the ductility. In order not 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 not particularly restricted, but it is desirable to be 0.1 mass ppm considering the melt production time in industry.

- S: not more than 20 mass ppm

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. And also, the lower limit of the S amount is not particularly restricted, but it is desirable to be 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

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 not restricted, but they are preferable to be 5 mass ppm and 3 mass ppm, respectively, considering the melt producing cost.

**[0014]** 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.

**[0015]** The alloy according to the invention has excellent strength and ductility at a high temperature region above 1000°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 being less in incorporation of impurities from a crucible and the vacuum degree of  $10^{-5}$  Torr.

#### EXAMPLE

**[0016]** 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 950–1200°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.

**[0017]** 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 the 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	<u>50</u>	0.9	0.6	9	4	Comparative Example
B	<u>50</u>	<u>31</u>	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	<u>25</u>	9.3	80	30	Comparative Example
G	65	9.1	<u>32.2</u>	60	25	Comparative Example
H	65	8.2	7.6	<u>110</u>	<u>70</u>	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	$\geq 99.9$	9.8	7.5	44	29	Example
M	54Ni-18Cr-3.0Mo-18.5Fe		-	-	-	Conventional Example

[0018] 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. And also, 54Ni-18Cr-3Mo alloy used as a heat-resistant material from the old time violently lowers the ductility above 1000°C and renders RA at 1200°C into 0%.

[0019] On the contrary, the invention alloys indicate  $RA \times TS \geq 10000$  (%·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)					RAxTS (%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

5 **[0020]** 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.

10 **Claims**

1. A Cr-based alloy having an excellent strength-ductility balance at higher temperatures, comprising Cr: not less than 60 mass%, C+N: not more than 20 mass ppm, S: not more than 20 mass ppm, O: not more than 100 mass ppm, O as an oxide: not more than 50 mass ppm, and the remainder being Fe and inevitable impurities.

15

20

25

30

35

40

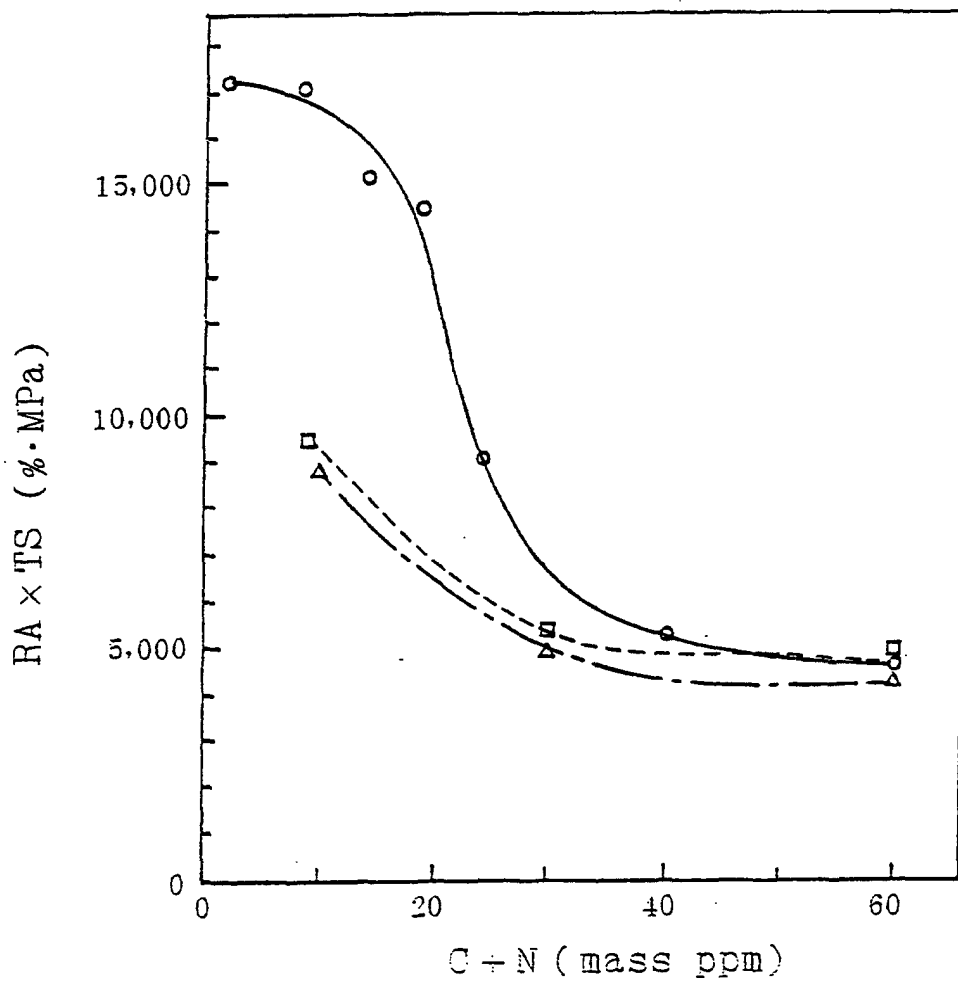
45

50

55

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



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP00/03399

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl <sup>7</sup> C22C27/06		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) Int.Cl <sup>7</sup> C22C27/06		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1926-1996 Toroku Jitsuyo Shinan Koho 1994-2000 Kokai Jitsuyo Shinan Koho 1971-2000 Jitsuyo Shinan Toroku Koho 1996-2000		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) WPI, JICST		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	Kenji ABIKO, "Chou Jundo Kinzoku wo Kenkyuu suru " 5. Kou Cr-Fe goukin no Chou Koujundoka, <i>Dai Kou Ken News</i> , VOL.43, NO.3 (April, 1999)	1
A	JP, 7-278718, A (KUBOTA Corporation), 24 October, 1995 (24.10.95), Claims; Column 2, lines 29-41 (Family: none)	1
Y	JP, 8-225899, A (Kenji ABIKO), 03 September, 1996 (03.09.96), Claims, column 2, lines 30-36; column 4, line 50 to column 5, line 9; column 6, lines 7-15 (Family: none)	1
A	JP, 48-102023, A (Showa Denko K.K.), 21 December, 1973 (21.12.73), Claims; page 4, lower left column, line 2 (Family: none)	1
A	EP, 597129, A (KAWASAKI STEEL CORPORATION), 30 April, 1993 (30.04.93), Claims	1
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family	
Date of the actual completion of the international search 26 July, 2000 (26.07.00)	Date of mailing of the international search report 08 August, 2000 (08.08.00)	
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer	
Facsimile No.	Telephone No.	

Form PCT/ISA/210 (second sheet) (July 1992)



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP00/03399

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	& WO 93/22471, A1      & JP, 6-33197, A & JP, 6-41696, A      & JP, 6-49603, A & JP, 6-49604, A  EP, 429796, A (KUBOTA CORPORATION), 28 September, 1990 (28.09.90), Claims & AU, 9063296, A      & JP, 3-162545, A & US, 5288228, A      & DE, 69024179, A & KR, 134182, A	1

Form PCT/ISA/210 (continuation of second sheet) (July 1992)