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

(11) EP 1 544 312 B1

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
15.09.2010 Bulletin 2010/37

(51) Int Cl.:
C21D 1/28 *(2006.01)* ***C22C 38/22*** *(2006.01)*
C22C 38/26 *(2006.01)*

(21) Application number: **04078288.0**

(22) Date of filing: **03.12.2004**

(54) **Method of producing heat-resistant high chromium ferritic/martensitic steel**

Verfahren zur Herstellung von hitzebeständigem Chrom-reichem ferritisch-martensitischem Stahl

Procédé de production d'acier ferritique-martensitique à haute teneur en chrome résistant à la chaleur

(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 MC NL PL PT RO SE SI SK TR

(30) Priority: **19.12.2003 KR 2003094059**

(43) Date of publication of application:
22.06.2005 Bulletin 2005/25

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- **PATENT ABSTRACTS OF JAPAN vol. 1995, no. 08, 29 September 1995 (1995-09-29) & JP 07 118812 A (HITACHI LTD), 9 May 1995 (1995-05-09)**
- **PATENT ABSTRACTS OF JAPAN vol. 1997, no. 01, 31 January 1997 (1997-01-31) & JP 08 225833 A (NIPPON STEEL CORP; FUJITA TOSHIO), 3 September 1996 (1996-09-03)**

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Printed by Jouve, 75001 PARIS (FR)

Description

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The present invention relates to a method for producing a heat-resistant high chromium ferritic/martensitic steel, which is applied to the pipes, tubes, and turbines of nuclear power plants, fossil power plants, and petrochemical plants.

2. Description of the Prior Art

[0002] Having superior thermal conductivity, high temperature strength, thermal fatigue strength, and a moderate price, a heat-resistant high chromium ferritic/martensitic steel is applied to tubes, pipes, turbines and so on of fossil power plants, nuclear power plants and the like.

[0003] The heat-resistant high chromium ferritic/martensitic steel is made of carbon, silicon, manganese, nickel, chromium, molybdenum, tungsten, vanadium, niobium, phosphorus, sulfur, nitrogen, and iron, and its composition and compositional ratio may be controlled according to its uses and required mechanical properties.

[0004] In accordance with an increase of the application temperature of a heat-resistant high chromium ferritic/martensitic steel, many studies have been conducted during the past decades to improve the creep rupture strength at high temperatures. The creep strength of the heat-resistant high chromium ferritic/martensitic steel is closely connected with stability of its microstructure, and thus, efforts have been made to develop a technology to form an ideal microstructure suitable to resist creep by controlling the alloying elements.

[0005] With respect to this, development of alloys has been mostly focused on two materials respectively, containing 9 % chromium and 12 % chromium. Additionally, a hardening mechanism of the heat-resistant high chromium ferritic/martensitic steel may be classified into a precipitation hardening, which is realized by forming stable precipitates, and a solid solution hardening, which is achieved by dissolving alloying elements in a matrix to form a solid solution. Studies have been made of a proper use of vanadium and niobium as an element which can be applied to a precipitation hardening to precipitate stable carbonitride. Further, conventionally, molybdenum has been frequently used as an element which can be applied to a solid solution hardening, but recently, tungsten has been used instead of molybdenum. Furthermore, materials containing cobalt, copper, or boron have been developed.
In recent years, efforts have been made to develop materials containing tantalum, rhenium, neodymium or those belonging to a rare-earth series. Currently, an alloy with a creep rupture strength of 180 Mpa at 600°C for 10^5 hours is in an experimental stage of development.

[0006] Meanwhile, a method of producing the heat-resistant high chromium ferritic/martensitic steel includes melting the material of the heat-resistant high chromium ferritic/martensitic steel to produce an ingot, hot working the ingot to produce an alloy with a predetermined shape, and heat treating the alloy.

[0007] Such a heat treatment, which is a principal factor determining the mechanical properties of the material of the heat-resistant high chromium ferritic/martensitic steel, serves to stabilize the microstructure of the material, and is comprised of the normalizing and tempering processes (refer to FIG. 1).

[0008] In the normalizing process, precipitates existing in the hot-worked material are mostly decomposed at high temperatures to allow the microalloying elements to exist in a solid solution state in a matrix, and the material is air cooled, and the microalloying elements are then existing in a supersaturated solid solution state when an austenite is transformed into a martensite. Typically, the normalizing process is conducted at 1050°C.

[0009] The tempering process, conducted after the completion of the normalizing process, serves to recover the dislocations while generating a great amount of precipitates from the microalloying elements existing in the supersaturated solid solution state through the normalizing process, thereby enabling the material to have desirable creep and impact properties. Stability of the precipitates is considered as one of the most important factors determining the high temperature creep rupture strength of the heat-resistant high chromium ferritic/martensitic steel. In order to enable the impact properties to be compatible with the high temperature strength to optimize a state of the material, a tempering temperature is determined at an A_{c1} temperature or less in consideration of the recovery of the dislocation and the generation of the precipitates. In detail, the conventional tempering process is conducted at 700 - 780°C.

[0010] In addition, recently, a method of heat treating a heat-resistant high chromium ferritic/martensitic steel containing cobalt has been suggested, in which a first tempering process is conducted at 500 - 620°C and a second tempering process is conducted at 690 - 740°C, but in this case, a low temperature tempering (first tempering) process is carried out so as to decompose any remaining austenite, which is not transformed to a martensite, after a normalizing process, and the second tempering process is conducted for the generation of precipitates and the recovery of the dislocations, which are a goal of a typical tempering process.

[0011] As described above, the heat-resistant high chromium ferritic/martensitic steel produced under conventional heat treatment conditions is disadvantageous in that the high temperature creep life is reduced because the microstructure is softened due to a martensite lath growth in its use at high temperatures, and thus, its application temperature is limited. Accordingly, there remains a need to develop a heat-resistant alloy assuring a desired creep strength even though it is used at a high temperature of 600°C or higher for a long time.

SUMMARY OF THE INVENTION

[0012] Therefore, the present invention has been made keeping in mind the above-mentioned disadvantages occurring in the prior arts, and an object of the present invention is to provide a method of heat treating the heat-resistant high chromium ferritic/martensitic steel, which has a superior creep rupture strength as well as impact properties similar to the case of adopting a conventional heat treatment.

[0013] The above object can be accomplished by providing a method of producing the heat-resistant high chromium ferritic/martensitic steel, which includes melting, hot working, and heat treatment processes. At this time, the heat treatment step includes a normalizing step at 1030 - 1100°C (first process), the first tempering step at 620 - 720°C (second process), and the second tempering step at 730 - 780°C (third process).

[0014] Components constituting the heat-resistant high chromium ferritic/martensitic steel used in the present invention are carbon, silicon, manganese, nickel, chromium, molybdenum, tungsten, vanadium, niobium, phosphorus, sulfur, nitrogen, and iron. In detail, the heat-resistant high chromium ferritic/martensitic steel includes 0.08 - 0.2 wt% carbon, 0.1 wt% or less silicon, 0.2 - 0.8 wt% manganese, 1.0 wt% or less nickel, 8.0 - 13.0 wt% chromium, 0.03 - 2.5 wt% molybdenum, 3 wt% or less tungsten, 0.1 - 0.3 wt% vanadium, 0.1 - 0.25 wt% niobium, 0.01 wt% or less phosphorus, 0.01 wt% or less sulfur, 0.04 - 0.10 wt% nitrogen, iron as the balance, and inevitable impurities.

Particularly, nitrogen plays an important role in forming the fine chromium carbonitride to maintain the creep strength, and thus, it is very important to properly maintain the content of nitrogen.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] The above and other objects, features and other advantages of the present invention will be more clearly understood from the following detailed description taken in conjunction with the accompanying drawings, in which:

FIG. 1 is a graph illustrating a conventional heat treating process in the course of producing a heat-resistant high chromium ferritic/martensitic steel;

FIG. 2 is a graph illustrating a heat treating process according to the present invention in the course of producing the heat-resistant high chromium ferritic/martensitic steel;

FIG. 3 is a TEM (transmission electron microscope) picture illustrating the chromium carbonitride generated when the heat-resistant high chromium ferritic/martensitic steel is subjected to the two-step tempering treatment; and

FIG. 4 shows the TEM pictures illustrating a variation of the martensite lath width before and after a creep test of the heat-resistant high chromium ferritic/martensitic steel.

DETAILED DESCRIPTION OF THE INVENTION

[0016] Hereinafter, a detailed description will be given of the present invention.

[0017] A heat treatment according to the present invention includes three steps (refer to FIG. 2).

[0018] In the first step, a normalizing treatment is conducted within a temperature range of 1030 - 1100°C. Since precipitates formed in the course of producing a heat-resistant alloy are mostly decomposed due to the normalizing treatment, the microalloying elements exist in a solid solution state in a matrix.

[0019] When a normalizing temperature is lower than the above temperature range, since the precipitates are incompletely decomposed, the alloying elements do not exist in a desirable solid solution state in the matrix, the fine precipitates are not formed, but the coarse and nonuniform precipitates are formed during a subsequent tempering treatment process, thereby deteriorating the mechanical properties. Additionally, when the normalizing temperature is higher than the above temperature range, austenite grains are grown in the form of a coarse grain, and thus, the ductility is reduced.

[0020] An air cooling process is conducted after the normalizing treatment. The microalloying elements, existing in the solid solution state in the matrix during the normalizing treatment, are present in a supersaturated solid solution state when the austenite is transformed into martensite due to the air cooling process.

[0021] After the normalizing treatment corresponding to the first process of the heat treatment, two-step tempering treatments are conducted, which serves to recover the dislocations while generating a great amount of precipitates, thereby improving the creep and impact properties of the heat-resistant alloy.

[0022] In the present invention, the tempering treatment is divided into the first tempering treatment corresponding to

the second process and the second tempering treatment corresponding to the third process.

[0023] The second process, that is, the first tempering treatment is conducted at 620 - 720°C. Since the first tempering treatment is conducted at 620 - 720°C, which is a temperature range lower than a conventional tempering temperature, relatively fine and stable chromium carbonitride can be generated. When the first tempering temperature is lower than the above-mentioned temperature range, a stable precipitate is insufficiently generated or the first tempering time is very long, and when the first tempering temperature is higher than the above-mentioned temperature range, a coarse precipitate is generated or chromium carbonitride is resolved to reduce the dispersion effect of the chromium carbonitride.

[0024] The fine precipitate generated within the above temperature range serves to efficiently suppress a movement of the dislocation and the growth of a martensite lath when a creep deformation occurs, thereby improving the creep rupture strength.

[0025] Successively, in the third process, the second tempering treatment is conducted at a temperature range of 730 - 780°C. When the second tempering treatment is conducted at a temperature lower than the above-mentioned temperature range, since the dislocation is insufficiently recovered, the impact ductility is poor, and when the second tempering treatment is conducted at a temperature higher than the above-mentioned temperature range, a martensite structure forms sub-grains to significantly reduce the strength because of an excess tempering process. Hence, the second tempering treatment is conducted within the above temperature range to assure the desired strength and ductility.

[0026] Even though coarse $M_{23}C_6$ carbide, generated during a conventional heat treatment, exists in a heat-resistant high chromium ferritic/martensitic steel produced through the above-mentioned heat treatment of the present invention, chromium carbonitride with a size of tens of nanometers are distributed to greatly stabilize the lath structure of the martensite as shown in FIG. 3.

[0027] As well, as shown in FIG. 4, when martensite structures of a high chromium ferritic/martensitic steel, in which chromium carbonitride is formed in the matrix, and a material, in which chromium carbonitride is not formed, are compared with each other after they are subjected to a creep test, it can be seen that in the case of the steel, in which chromium carbonitride is formed (upper three pictures in FIG. 4), the growth of the martensite lath width is significantly suppressed at both the head (no stress) and the gauge (under stress) of the creep test piece. That is to say, softness due to a creep deformation is delayed by the formation of chromium carbonitride, thereby improving the creep rupture strength.

[0028] Having generally described this invention, a further understanding can be obtained by reference to certain specific examples, comparative examples, and experimental examples which are provided herein for the purposes of illustration only and are not intended to be limiting unless otherwise specified.

EXAMPLE 1: Production of a heat-resistant high chromium ferritic/martensitic steel

[0029] An alloy with a composition as described in Table 1 was prepared as a test sample to be used in examples. The alloy was shaped as a 30 kg ingot in a vacuum induction melting furnace. The ingot was hot worked at 1100°C to gain a thickness of 15 mm.

[0030] Subsequently, a heat treatment was conducted. In detail, the alloy was normalized at 1050°C for 1 hour, and then air-cooled.

[0031] Successively, a tempering treatment was conducted through two steps. In detail, the normalized alloy was subjected to the first tempering treatment at 700°C for 2 hours, air-cooled, subjected to the second tempering treatment at 750°C for 1 hour, and air-cooled to produce a heat-resistant high chromium ferritic/martensitic steel.

TABLE 1 Chemical composition

Chemical component (wt%)											
C	Si	Mn	Ni	Cr	Mo	V	Nb	P	S	N	Fe
0.15	0.061	0.47	0.45	10.01	1.29	0.200	0.210	0.001	0.001	0.079	Balance

COMPARATIVE EXAMPLE 1: Production of a heat-resistant high chromium ferritic/martensitic steel according to a conventional heat treatment

[0032] The procedure of example 1 was repeated with the exception of a tempering treatment being conducted through one step, unlike the case of example 1 in which the tempering treatment was conducted through two steps, that is, the first and second tempering treatments, thereby producing an alloy with the same composition as that of example 1. At this time, the tempering treatment conditions were 750°C and 2 hours.

EXPERIMENTAL EXAMPLE 1: Tension and impact tests

[0033] These tests were conducted to evaluate the room- and high-temperature tensile properties and the roomtemperature impact properties of the heat-resistant high chromium ferritic/martensitic steel according to example 1 and comparative example 1.

[0034] The tension test was carried out using an Instron 4505. In this regard, a tension test piece was shaped into a plate with a length of 100 mm, a gauge length of 28.5 mm, and a width of 6.25 mm. The high temperature tension test was conducted at 600 ± 3°C, and all the tension tests were repeated three times to obtain an average of the measured values.

[0035] The impact test was executed using an impact testing machine, manufactured by SATEC Ltd., at room temperature.

At this time, the impact test piece had a length of 55 mm, a width of 10 mm, and a height of 10 mm, and also had a V-notch formed at the center thereof. The impact test was repeated three times to obtain an average of the measured values.

[0036] The results are described in the following Table 2.

TABLE 2 Room and high temperatures tension and impact tests

	Room temperature			600°C			Charpy V impact absorbed energy (J)
	Yield strength (MPa)	Tensile strength (MPa)	Elongation (%)	Yield strength (MPa)	Tensile strength (Mpa)	Elongation (%)	
Ex.1	682	848	19	413	451	28	131
Co.Ex.1	649	824	21	406	442	28	137

[0037] As shown in the Table 2, the heat-resistant alloy of example 1 according to the present invention had a relatively increased yield and tensile strengths at both the room temperature and a high temperature (600°C) in comparison with those of comparative example 1.

Furthermore, the elongation was the same at a high temperature but slightly lower at room temperature.

[0038] Meanwhile, the impact properties differed little from each other at room temperature.

[0039] Through the above description, it can be seen that the heat-resistant alloy produced according to the present invention has superior tensile properties at both the room and high temperatures, which are believed to be achieved by the two-step tempering treatments according to the present invention.

EXPERIMENTAL EXAMPLE 2: Measurement of the creep rupture strength

[0040] The following procedure was conducted to measure the creep rupture strengths of the heat-resistant high chromium ferritic/martensitic steels according to example 1 and comparative example 1.

[0041] A creep test piece was shaped into a rod with a length of 90 mm, a gauge length of 30 mm, and a diameter of 6 mm. The creep rupture strength was measured using a creep testing machine, manufactured by Power Engineering Corp., according to a constant load test. The test temperature was adjusted to 600 ± 3°C, and the displacement according to the deformation was measured using a linear variable differential transformer (LVDT).

[0042] The results are described in Table 3.

[0043] As shown in Table 3, the creep rupture life of the heat-resistant alloy produced according to example 1 (two-step tempering treatment) was improved by about 30 % or more in comparison with that of the heat-resistant alloy produced according to comparative example 1 (one-step tempering treatment). This is believed to be achieved by the two-step tempering treatments according to the present invention.

TABLE 3 High temperature creep test

Example		Comparative example	
Load(Mpa)	Rupture life (hour)	Load (MPa)	Rupture life (hour)
210	978	210	381
195	2500	195	1385
180	5714	180	4504

[0044] As apparent from the above description, the present invention is advantageous in that a tempering treatment is conducted under predetermined conditions through two steps to desirably distribute the chromium carbonitride with a size of tens of nanometers to greatly stabilize the structure of the martensite lath, thereby producing a heat-resistant high chromium ferritic/martensitic steel with a superior creep rupture strength as well as superior impact properties.

[0045] The heat-resistant high chromium ferritic/martensitic steel is usefully applied to nuclear fuel claddings, heat transfer tubes, and pipes of nuclear power plants, and pipes, tubes, turbines and the like for the boilers of fossil power plants, which must have a superior creep rupture strength and impact properties at a high temperature of about 600°C.

[0046] The present invention has been described in an illustrative manner, and it is to be understood that the terminology used is intended to be in the nature of a description rather than of limitation. Many modifications and variations of the present invention are possible in light of the above teachings. Therefore, it is to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

Claims

1. A method of producing heat-resistant high chromium steel which comprises 0.08 - 0.2 wt% carbon, 0.1 wt% or less silicon, 0.2 - 0.8 wt% manganese, 1.0 wt% or less nickel, 8.0 - 13.0 wt% chromium, 0.03 - 2.5 wt% molybdenum, 3 wt% or less tungsten, 0.1 - 0.3 wt% vanadium, 0.1 - 0.25 wt% niobium, 0.01 wt% or less phosphorus, 0.01 wt% or less sulphur, 0.04 - 0.10 wt% nitrogen, and iron as a balance, which method includes melting, hot working, and heat treatment processes, wherein the heat treatment process consists of:

   a normalizing step at 1030 - 1100 °C (first process);
   the first tempering step at 620 - 720 °C (second process); and
   the second tempering step at 730 - 780 ° C (third process).

2. The method as set forth in claim 1, further comprising of an air cooling step after the normalizing step is conducted at 1030 - 1100 °C.

3. The method as set forth in claim 1, further comprising of an air cooling step after the first tempering step is conducted at 620 - 720 °C.

4. The method as set forth in claim 1, further comprising of an air cooling step after the second tempering step is conducted at 730 - 780 °C.

Patentansprüche

1. Verfahren zum Herstellen eines hitzebeständigen, hoch chromhaltigen Stahls, welcher 0,08 bis 0,2 Gew.% Kohlenstoff, 0,1 Gew.% oder weniger Silizium, 0,2 bis 0,8 Gew.% Mangan, 1,0 Gew.% oder weniger Nickel, 8,0 bis 13,0 Gew.% Chrom, 0,3 bis 2,5 Gew.% Molybdän, 3 Gew.% oder weniger Wolfram, 0,1 bis 0,3 Gew.% Vanadium, 0,1 bis 0,25 Gew.% Niob, 0,01 Gew.% oder weniger Phosphor, 0,01 Gew.% oder weniger Schwefel, 0,04 bis 0,10 Gew. % Stickstoff, und Eisen als einen Restbetrag umfasst, wobei das Verfahren Schmelz-, Warmbearbeitungs- und Heißbehandlungsprozesse umfasst, wobei der Heißbehandlungsprozess besteht aus:

   einem Normierungsschritt bei 1030 bis 1100°C (erster Prozess);
   dem ersten Härtungsschritt bei 620 bis 720°C (zweiter Prozess); und
   dem zweiten Härtungsschritt bei 730 bis 780°C (dritter Prozess).

2. Verfahren nach Anspruch 1, ferner mit einem Luftkühlungsschritt, nachdem der Normierungsschritt bei 1030 bis 1100°C durchgeführt worden ist.

3. Verfahren nach Anspruch 1, ferner mit einem Luftkühlungsschritt, nachdem der erste Härtungsschritt bei 620 bis 720°C durchgeführt worden ist.

4. Verfahren nach Anspruch 1, ferner mit einem Luftkühlungsschritt, nachdem der zweite Härtungsschritt bei 730 bis 780°C durchgeführt worden ist.

Revendications

1. Procédé de production d'acier à haute teneur en chrome thermorésistant qui comprend 0,08 à 0,2 % en poids de carbone, 0,1 % en poids ou moins de silicium, 0,2 à 0,8 % en poids de manganèse, 1,0 % en poids ou moins de nickel, 8,0 à 13,0 % en poids de chrome, 0,03 à 2,5 % en poids de molybdène, 3 % en poids ou moins de tungstène, 0,1 à 0,3 % en poids de vanadium, 0,1 à 0,25 % en poids de niobium, 0,01 % en poids ou moins de phosphore, 0,01 % en poids ou moins de soufre, 0,04 à 0,10 % en poids d'azote et le reste en tant que fer, le procédé comprenant les processus de fusion, formage à chaud et traitement thermique, où le processus de traitement thermique consiste en :

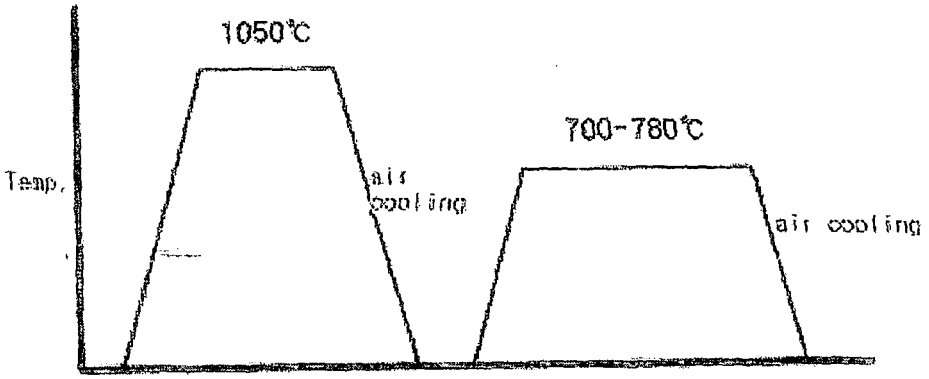
   une étape de normalisation à 1 030 à 1 100 °C (premier processus) ;
   la première étape de revenu à 620 à 720 °C (deuxième processus) ; et
   la seconde étape de revenu à 730 à 780 °C (troisième processus) .

2. Procédé selon la revendication 1, comprenant en outre une étape de refroidissement par air après l'étape de normalisation conduite à 1 030 à 1 100 °C.

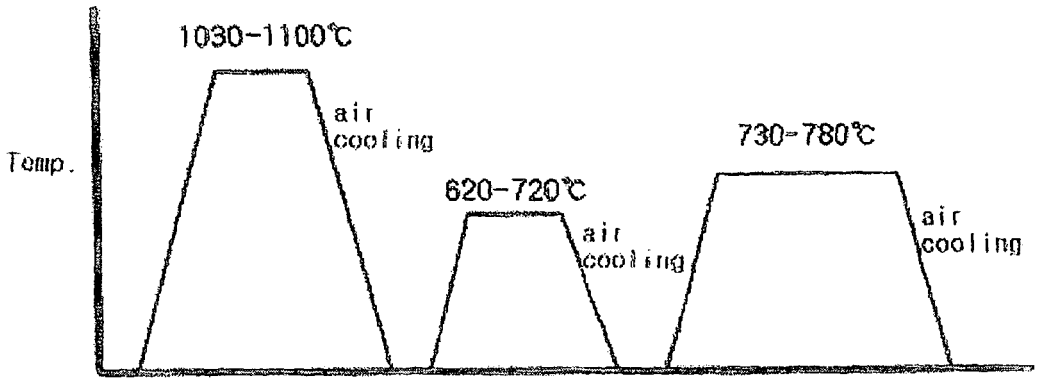
3. Procédé selon la revendication 1, comprenant en outre une étape de refroidissement par air après la première étape de revenu conduite à 620 à 720 °C.

4. Procédé selon la revendication 1, comprenant en outre une étape de refroidissement par air après la seconde étape de revenu conduite à 730 à 780 °C.

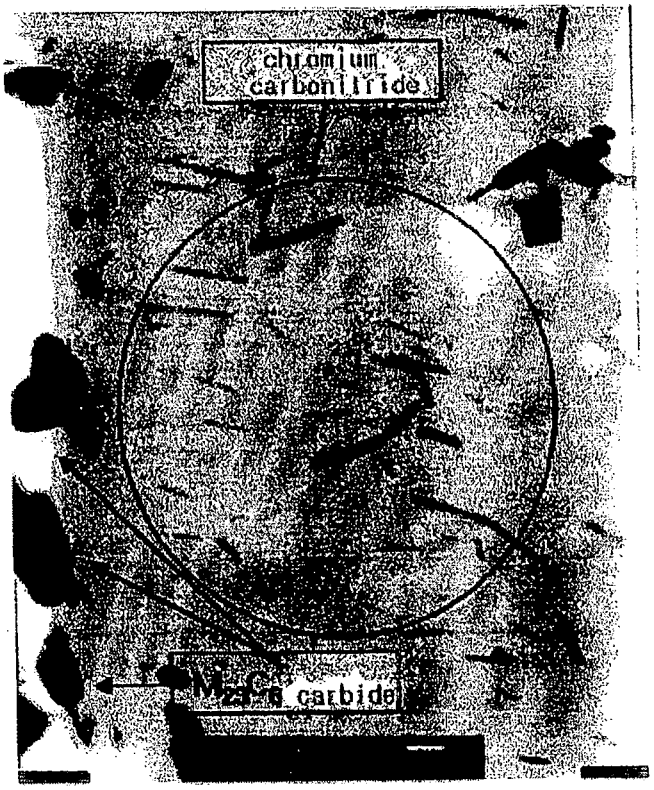
[FIG. 1]


1050℃
700-780℃
Temp.
air cooling
air cooling

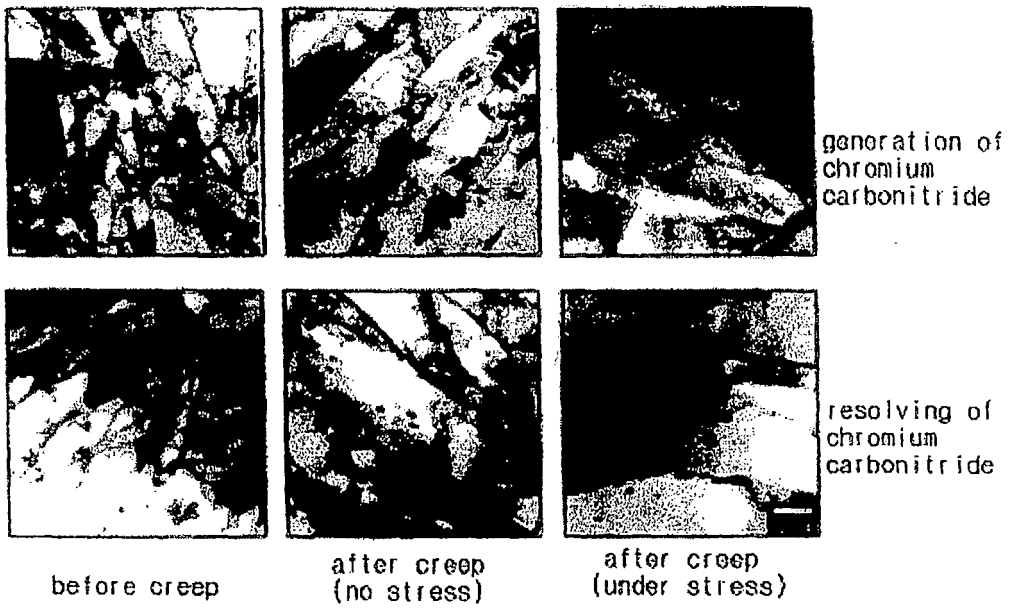
[FIG.2]


1030-1100℃
air cooling
730-780℃
620-720℃
air cooling
air cooling
Temp.

[FIG. 3]



[FIG. 4]


generation of chromium carbonitride
resolving of chromium carbonitride
before creep
after creep (no stress)
after creep (under stress)