(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
12 September 2008 (12.09.2008)

PCT

(10) International Publication Number
WO 2008/106978 A1

(51) International Patent Classification:
*C22C 38/00* (2006.01)

(21) International Application Number:
PCT/DK2008/050049

(22) International Filing Date:
28 February 2008 (28.02.2008)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
07103496.1 5 March 2007 (05.03.2007) EP
60/905,175 5 March 2007 (05.03.2007) US

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(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Published:**
— *with international search report*

# (54) Title: MARTENSITIC CREEP RESISTANT STEEL STRENGTHENED BY Z-PHASE

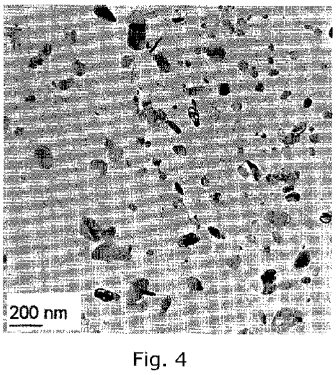

Fig. 4

(57) **Abstract:** The present invention relates to steel alloys having a martensitic or martensitic- ferritic structure and comprising Z-phase (CrXN) particles, where X is one or more of the elements V, Nb, Ta, and where the Z-phase particles have an average size of less than 400 nm. The alloy comprises by wt % the following components: 9 to 15% Cr, 0.01-0.20% N, C in an amount less than 0.1%, one or more of: 0.01- 0.5%V,0.01-1%Nb, 0.01-2%Ta, and a balance being substantially iron and inevitable impurities. The invention further relates to a method of manufacturing such a steel alloy, a component comprising such a steel alloy, and to the use of such a steel alloy for high temperature components.

# MARTENSITIC CREEP RESISTANT STEEL STRENGTHENED BY Z-PHASE

## FIELD OF THE INVENTION

The present invention relates to martensitic or martensitic-ferritic steel alloys and in particular to creep resistant alloys to be used for high temperature components. The invention further relates to manufacturing of such steels.

## BACKGROUND OF THE INVENTION

In the field of steam power plants there is strong focus on improving the efficiency of the plants by increase of operating steam temperature and pressure. A main limiting factor is the high temperature properties of materials used in the boilers, steam lines and turbines. These materials have to be designed to operate at high temperatures and stresses for prolonged times, so high creep strength and oxidation resistances are needed in order to keep degradation to a minimum. Tempered martensitic steel alloys offer the best combination of creep strength, oxidation resistance, thermal expansion coefficient and yield strength.

Over the last two decades, several 9%Cr martensitic steel alloys with improved creep strength have been developed. These alloys have enabled increases of steam parameters from typically 250 bar and 540°C up to the currently best available 300 bar and 600°C, corresponding to 10% improved efficiency. All contents are shown by weight percent here and in the following.

Recently, martensitic steel alloys have been under development to enable even higher steam parameters. In order to increase the steam temperature to above 600°C, the alloys need improved creep strength and a Cr content of 11-12% for improved oxidation resistance. Creep testing of the new 11-12%Cr alloys for a few thousand hours indicated improved creep strength. However, prolonged testing showed unexpected breakdowns in creep strength to strength levels below those of the currently available steels.

The martensitic steels contain minor amounts of elements like C, N, V, Nb which form precipitate particles such as $M_{23}C_6$ carbides and MX (V,Nb)-carbonitrides. These precipitate particles provide high creep strength by particle strengthening, but during prolonged exposure to high temperature the $M_{23}C_6$ carbides will coarsen and loose their particle strengthening effect. The coarsening rate of MX particles is low and they will remain fine and provide a major contribution to high long-term creep strength.

However, studies have shown that the fine MX particles may be dissolved and replaced by Z-phase particles, Cr(V,Nb)N, during long-term testing at high temperatures. The Z-phase precipitation is found to consist of slow continuous nucleation and fast growth. This results in a large average size of Z-phase particles, although small and large Z-phase particles may be observed to coexist in the same specimen. , Z-phase with large average particle size provides severely reduced particle strengthening compared to the fine MX particles. Thus, Z-phase precipitation can explain the observed breakdowns in long-term strength of new 11-12%Cr steels.

Z-phase nitride has since long been known from austenitic stainless steels where it may precipitate as very fine particles, which remain fine and contribute to high creep strength. However, in martensitic steels Z-phase was always found to grow to large average particle sizes.

The above mentioned studies are described in "Behaviour of Z phase in 9-12%Cr steels", H.K. Danielsen and J. Hald, Energy Materials, 2006, Vol. 1, No. 1.

## OBJECT OF THE INVENTION

It is an object of the present invention to provide a martensitic or martensitic-ferritic steel alloy with improved long-term creep properties compared to presently known materials.

It is another object of the present invention to provide a martensitic or martensitic-ferritic steel alloy with improved corrosion resistance compared to presently known materials.

It is an object of preferred embodiments of the present invention to provide a martensitic or martensitic-ferritic steel alloy in which the good creep properties can be combined with a high corrosion resistance.

It is a further object of the present invention to provide an alternative to the prior art.

SUMMARY OF THE INVENTION

The above described object and several other objects are intended to be obtained in a first aspect of the invention by providing a steel alloy comprising by wt % the following components: 9 to 15% Cr, 0.01-0.20% N, C in an amount less than 0.1%, one or more of: 0.01-0.5%V, 0.01-1%Nb, 0.01-2%Ta, and a balance being substantially iron and inevitable impurities, said steel alloy having a martensitic or martensitic-ferritic structure and comprising Z-phase (CrXN) particles, where X is one or more of the elements V, Nb, Ta, and where the Z-phase particles have an average size of less than 400 nm, such as less than 300 nm, such as less than 200 nm, such as less than 100 nm.

The present invention is based on the idea that the precipitation of Z-phase particles should be accelerated to obtain a large number of particles and thereby a small particle size. The Z-phase particles may precipitate either during heat treatment as a part of the manufacturing or during service exposure. It may be advantageous e.g. with respect to quality control before use, if the particles precipitate already during the manufacturing of the steel.

In embodiments of the invention, the steel alloy may further comprise one or more of the following components: Co in an amount less than 8%, one or more of Mo and W in an amount less than 4%, one or more of Mn, Ni and Cu in an amount less than 3%, Si in an amount less than 2%, and B in an amount less than 0.04%.

A second aspect of the invention relates to a method of manufacturing a steel alloy as described above, said method comprising the steps of melting the components, molding the melt to form a material, subjecting the molded material to a solution temperature between 1000 °C and 1300 °C, and subjecting the molded material to a tempering treatment at a temperature between 500 °C and 850 °C. The duration of the manufacturing steps depends on the size of the component being manufactured and on specific requirements for toughness and tensile strength. For thin tubes the holding times at solution and tempering temperatures may be in the order of 15 min, whereas for a massive 40 ton turbine casing the holding times may amount to several tens of hours.

A third aspect of the invention relates to a high temperature component comprising a steel alloy as described above. By high temperature component is meant a component that is designed to be exposed to temperatures above 500 °C.

A fourth aspect of the invention relates to the use of a steel alloy as described above for high temperature components. It may typically be for components in power generation boilers or turbines, nuclear power generation facilities, jet engines, or components in chemical industry.

The first, second, third and fourth aspect of the present invention may each be combined with any of the other aspects. These and other aspects of the invention will be apparent from and elucidated with reference to the embodiments described hereinafter.

## BRIEF DESCRIPTION OF THE FIGURES

The steel alloy according to the invention will now be described in more detail with regard to the accompanying figures. The figures show one way of implementing the present invention and is not to be construed as being limiting to other possible embodiments falling within the scope of the attached claim set.

Figure 1 is an example of experimental results from creep tests on a prior art steel.

Figure 2 shows precipitates in a steel alloy comprising MX and $M_{23}C_6$ particles.

Figure 3 shows precipitates in a steel alloy comprising $M_{23}C_6$ and coarse Z-phase particles.

Figure 4 shows precipitates in a steel alloy according to the present invention comprising fine Z-phase particles. The figure shows the microstructure after exposure to 650°C for 17,000 hours.

Figure 5 shows very fine Z-phase particles in Steel 1 of table 1 after exposure to 650°C for 3000 hours.

## DETAILED DESCRIPTION OF AN EMBODIMENT

Components for use in power plants should be designed to operate at high temperatures and stresses for very long times, preferably more than 30 years. It is not practical to test new materials for so long, and therefore long-term properties are estimated by extrapolating results from shorter-term tests. Double logarithmic plots of test stress vs. rupture time normally show smooth curves, but many 11-12%Cr steels suffer a breakdown in long-term strength and the curves bend after several thousand hours of testing. An example of such bent curves is given in figure 1, showing creep test results for a steel with 0.1%C, 11%Cr, 3%Co, 3%W, and minor contents of V, Nb and N.

High long-term creep strength of steel alloys has recently been obtained by compositions resulting in precipitation of fine MX nitride particles in the form (V,Nb)N in addition to coarser $M_{23}C_6$ carbide particles. An example of such an alloy is given in figure 2, which shows particles in a steel with 0.1%C, 9%Cr, 1.5%W and minor content of V, Nb and N.

However, recent studies of several martensitic steels after long term operation at high temperatures have shown that Z-phase nitride particles may precipitate and dissolve the fine MX particles. Growth of the Z-phase results in large average particle size which provides severely reduced particle strengthening. In steels with 11-12%Cr, the Z-phase precipitation is significantly accelerated compared to steels with 9%Cr. This causes the breakdown in long-term creep strength as shown in figure 1. An example of a coarse Z-phase particle in a steel with 11%Cr, 2.5%W, 2.5%Co and minor content of V, Nb and N is shown in figure 3.

The said studies of Z-phase in martensitic steels included the development of a thermodynamic model, which enables the prediction of the Z-phase thermodynamic stability and precipitation rate as a function of alloy composition. The model predicts that increasing the Cr content accelerates Z-phase precipitation, and in order to retard Z-phase precipitation beyond normal operation times (30 years), the Cr content must be limited to 9%. Thus, it is not possible to combine high creep strength obtained by MX precipitate particles with high oxidation resistance by Cr contents of 11% and above.

In order to obtain both high creep strength and high oxidation resistance, possibilities to control Z-phase precipitation in order to form fine Z-phase precipitates which remain fine in martensitic steel were explored. The developed thermodynamic model was used to determine an alloy composition, which would result in martensitic steel, wherein the precipitation rate of Z-phase would be strongly enhanced compared to other 11-12%Cr steels. In such steel the Z-phase would be prevented from growing to large particles, thus enabling a fine precipitation of Z-phase with small average particle size. Based on theoretical considerations, the coarsening rate of Z-phase particles is lower than for MX particles, and fine Z-phase particles should remain fine after long-term exposure for more than 100,000 hours at temperatures above 600°C.

An alloy composition based on 12%Cr, low carbon content and balanced additions of Nb and N was used to produce a first model steel for preliminary investigations. The model steel precipitates fine Z-phase particles, which remain fine after exposure up to 17,000 hours at 650°C. Figure 4 shows fine Z-phase particles with an average size of 80 nm in the model alloy with 0.04%C; 12%Cr; 1%Mo, 1%Ni, 0.5%Co, 0.4%Nb and 0.07%N after 17,000hours at 650°C. The fine Z-phase particles will thus contribute to high long-term creep strength of the alloy, and it will be possible to combine high creep strength by Z-phase precipitation with high oxidation resistance from a 12%Cr content in the same alloy.

In order to attain the defined precipitation of fine Z-phase particles in the steel alloy, it is necessary to obtain a martensitic or martensitic-ferritic microstructure, as this will provide a high density of nucleation sites for fine precipitate particles. The martensitic or martensitic-ferritic microstructure is obtained by subjecting a molded steel alloy to a solution temperature where the microstructure consists of austenite or austenite and δ-ferrite. This microstructure is best obtained at solution temperatures between 1000°C and 1300°C. The holding time at the solution temperature is determined according to the component size and may vary from a few minutes to several hours. Upon cooling from the solution temperature, the austenitic part of the microstructure transforms into martensite, thus a martensitic or a martensitic-ferritic microstructure is formed. In order to obtain good toughness, it is necessary to limit the amount of δ-ferrite formed during solution heat treatment. This is done by balancing the composition of the steel alloy as described below.

The martensite formed after solution treatment is brittle. In order to eliminate this brittleness and achieve a good balance between strength and toughness, the steel alloy should be subjected to a tempering treatment at a temperature of at least 500°C. If the tempering temperature exceeds 850°C, part of the microstructure may transform into austenite, which could result in low toughness. Holding time at the tempering temperature depends on the specific requirements for strength and toughness. For thin tubes it may be as low as 30 minutes, whereas large massive turbine forgings may require several tens of hours.

Alloy compositions based on 12% Chromium, low Carbon, balanced additions of Nb and N, and balanced additions of Mo, W and Co, Cu, Ni for further strengthening were used to produce test steels for investigations. Compositions of the two test steels are shown in table 1. After molding and rolling, Steel 1 was subjected to a heat treatment consisting of solution treatment at 1050°C for one hour and cooled by air followed by tempering at 750°C for two hours. This steel has a microstructure consisting of tempered martensite and δ-ferrite. Long term exposure to 650°C for 3000 hours resulted in precipitation of inter-metallic ($Fe_2W$) Laves phase and very fine Z-phase particles as shown in figure 5. The obtained Z-phase particles are much finer than those obtained in the preliminary steel shown in figure 4 and should thus provide a larger contribution to creep strength.

After molding and rolling, Steel 2 was subjected to a heat treatment consisting of solution treatment at 1100°C for one hour and cooled by air followed by tempering at 650°C for 24 hours. This steel has a microstructure consisting of tempered martensite.

Further alloy compositions are shown as steel 3 and 4 in table 1. Target of steel 3 is to demonstrate the combined strengthening effect of high Tungsten and CrNbN Z-phase. Target of steel 4 is to demonstrate the strengthening effect of CrTaN Z-phase.

| Composition, wt% | Steel 1 | Steel 2 | Steel 3 | Steel 4 |
|---|---|---|---|---|
| C | 0.004 | 0.0032 | 0.003 | 0.003 |
| Si | 0.35 | 0.29 | 0.3 | 0.3 |
| Mn | 0.49 | 0.47 | 0.5 | 0.5 |
| Cr | 11.96 | 11.60 | 12 | 12 |
| Mo | 0.19 | 0.20 | - | - |
| W | 2.51 | 2.42 | 3 | 3 |
| Ni | 0.62 | 0.46 | 1 | 1 |
| Co | 3.00 | 4.82 | 6 | 6 |
| Cu | 1.01 | 0.92 | - | - |
| Nb | 0.43 | 0.26 | 0.27 | - |
| Ta | - | - | - | 0.64 |
| N | 0.06 | 0.04 | 0.04 | 0.04 |
| B | 0.0070 | 0.0029 | 0.005 | 0.005 |

Table 1. Chemical composition of test steels, weight percent, bal. Fe,

In steel alloys according to the present invention, it is essential to use a material containing the specified components in specific amounts. The features of each component and their contents are described in detail below.

Chromium is necessary to obtain high oxidation and corrosion resistance of the steel, thus an amount of at least 9% is necessary. Furthermore, it is a necessary component in order to obtain fine precipitation of Z-phase particles. However, too high amount of Chromium will result in the formation of excess amount of δ-ferrite. Thus the maximum limit of Chromium is set to 15%.

Nitrogen enhances the hardenability of steels with low carbon content and contributes to the formation of a martensitic structure. Since Nitrogen is a necessary component of Z-phase, it is added in an amount of at least 0.01%. Too high amount of Nitrogen may result in the formation of porosities in the molded material, and thus the content is limited to a maximum of 0.20%.

Carbon in too high amount will result in the formation of $M_{23}C_6$ carbides, which will consume Cr from the steel and delay Z-phase precipitation. Furthermore, it may form MX carbides rich in Nb or Ta and prevent the formation of Z-phase based on these elements. Thus the Carbon content is limited to a maximum of 0.1%.

Vanadium, Niobium and Tantalum are essential components to form the Z-phase in combination with Chromium and Nitrogen. Thus, one or more of these components should be added to the steel in amounts higher than 0.01%. The maximum content of these components is balanced with the content of Nitrogen in order to avoid coarsening of the Z-phase. Thus, the maximum content of the components are set to 0.5% for Vanadium, 1% for Niobium and 2% for Tantalum.

Molybdenum and Tungsten are added to provide further solid solution hardening or particle strengthening by formation of inter-metallic Laves phase $Fe_2(Mo,W)$. Too high an amount of each component may result in the formation of an excess amount of δ-ferrite and reduction of the toughness of the steel. Thus the content of Molybdenum or Tungsten is set to a maximum of 4%.

Manganese, Nickel, Cobalt or Copper are added in order to suppress the formation of excessive amounts of δ-ferrite. Too high amounts of each element may result in limited ability to temper the alloys or reduced ductility. Thus, the maximum amount of Cobalt is set to 8%, and the maximum content of each of the components Manganese, Nickel or Copper is set to 3%.

Silicium is added to improve steelmaking and to enhance oxidation and corrosion resistance. However, too high an amount of Silicium may result in degradation of the toughness. Thus the maximum content of Silicium is set to 2%.

Boron may enhance hardenability of the steel and contributes to high creep strength through grain boundary strengthening. However, too high an amount may result in degradation of the toughness. Thus, the maximum limit of Boron is set to 0.04%.

Steel alloys according to the present invention are particularly advantageous for high temperature components in fossil fired steam power plants. However, use in other fields of applications is also covered by the scope of the present invention.

Steel alloys according to the present invention are typically homogenous at a macroscopic level. However, in-homogenous steel structures are also covered by the scope of the present invention. Such in-homogeneities could e.g. be a variation in particle size across the thickness of a component.

Although the present invention has been described in connection with the specified embodiments, it should not be construed as being in any way limited to the presented examples. The scope of the present invention is set out by the accompanying claim set. In the context of the claims, the terms "comprising" or "comprises" do not exclude other possible elements or steps. Also, the mentioning of references such as "a" or "an" etc. should not be construed as excluding a plurality. Furthermore, individual features mentioned in different claims, may possibly be advantageously combined, and the mentioning of these features in different claims does not exclude that a combination of features is not possible and advantageous.

## CLAIMS

1. A steel alloy comprising by wt % the following components:

- 9 to 15% Cr,
- 0.01-0.20% N,
- C in an amount less than 0.1%,
- one or more of: 0.01-0.5%V, 0.01-1%Nb, 0.01-2%Ta, and
- a balance being substantially iron and inevitable impurities,

said steel alloy having a martensitic or martensitic-ferritic structure and comprising Z-phase (CrXN) particles, where X is one or more of the elements V, Nb, Ta, and where the Z-phase particles have an average size of less than 400 nm, such as less than 300 nm, such as less than 200 nm, such as less than 100 nm.

2. A steel alloy according to claim 1, further comprising one or more of the following components:

- Co in an amount less than 8%,
- one or more of Mo and W in an amount less than 4%,
- one or more of Mn, Ni and Cu in an amount less than 3%,
- Si in an amount less than 2%, and
- B in an amount less than 0.04%.

3. A method of manufacturing a steel alloy according to claim 1 or 2, said method comprising the steps of:

- melting the components
- molding the melt to form a material
- subjecting the molded material to a solution temperature between 1000 °C and 1300 °C, and
- subjecting the molded material to a tempering treatment at a temperature between 500 °C and 850 °C,

wherein the duration of the solution and tempering treatments depends on the size of the component being manufactured and on predefined requirements for toughness and tensile strength.

4. A high temperature component comprising a steel alloy according to claim 1 or 2.

5. Use of a steel alloy according to claim 1 or 2 for high temperature components.

6. Use of a steel alloy according to claim 5 for components in power generation boilers or turbines, nuclear power generation facilities, jet engines, or components in chemical industry.

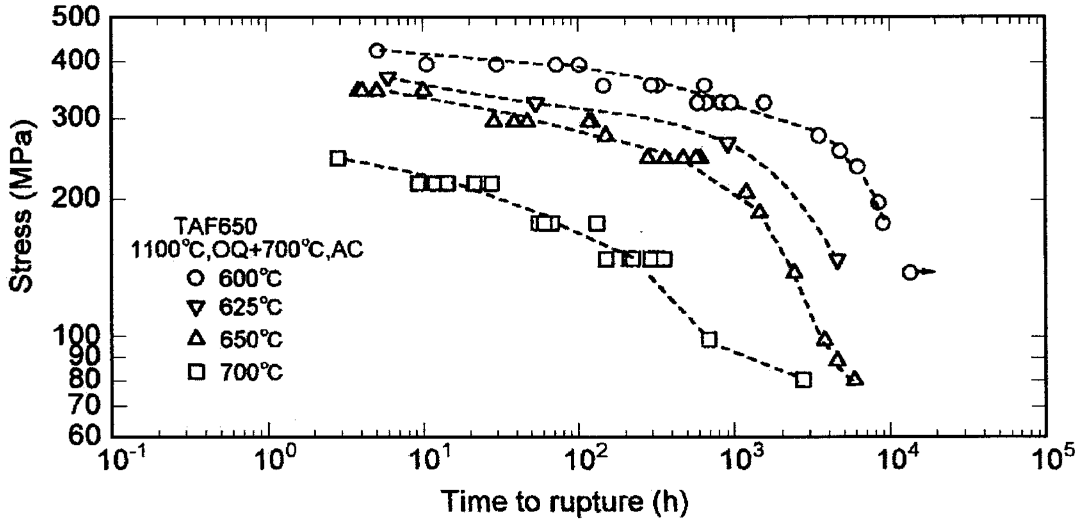
500
400
300
200
100
90
80
70
60
Stress (MPa)
TAF650
1100℃,OQ+700℃,AC
○ 600℃
▽ 625℃
△ 650℃
□ 700℃
$10^{-1}$
$10^{0}$
$10^{1}$
$10^{2}$
$10^{3}$
$10^{4}$
$10^{5}$
Time to rupture (h)

Fig. 1

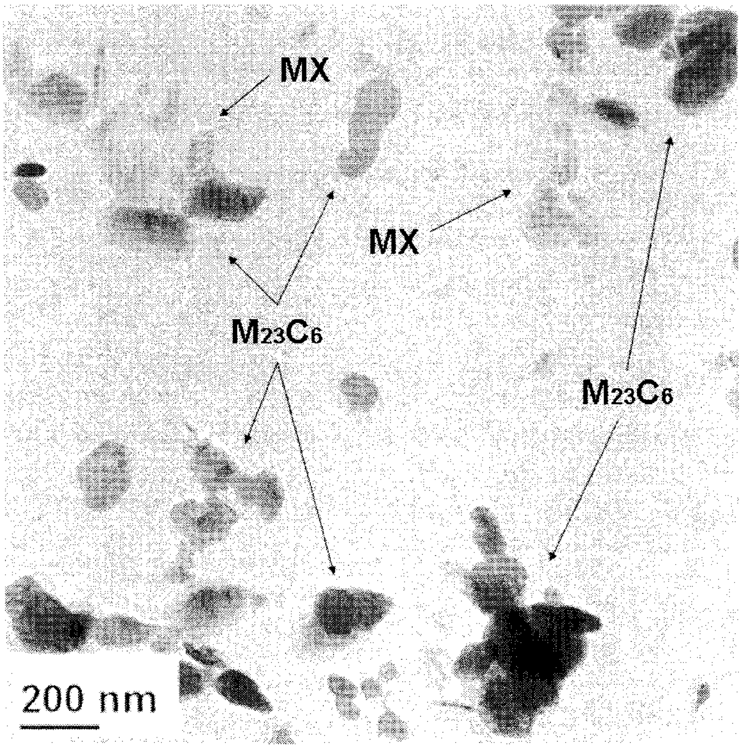
MX
MX
$M_{23}C_6$
$M_{23}C_6$
200 nm

Fig. 2

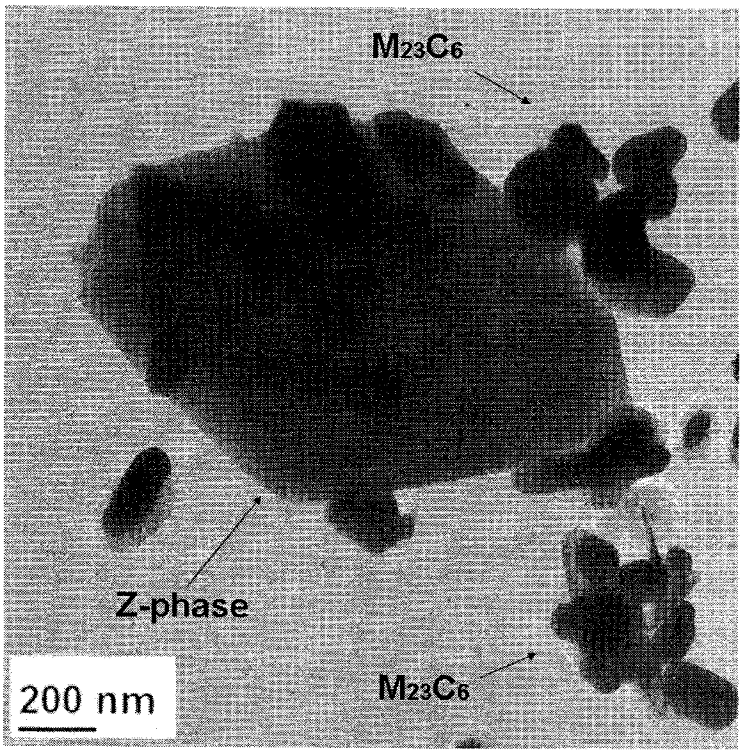

Fig. 3

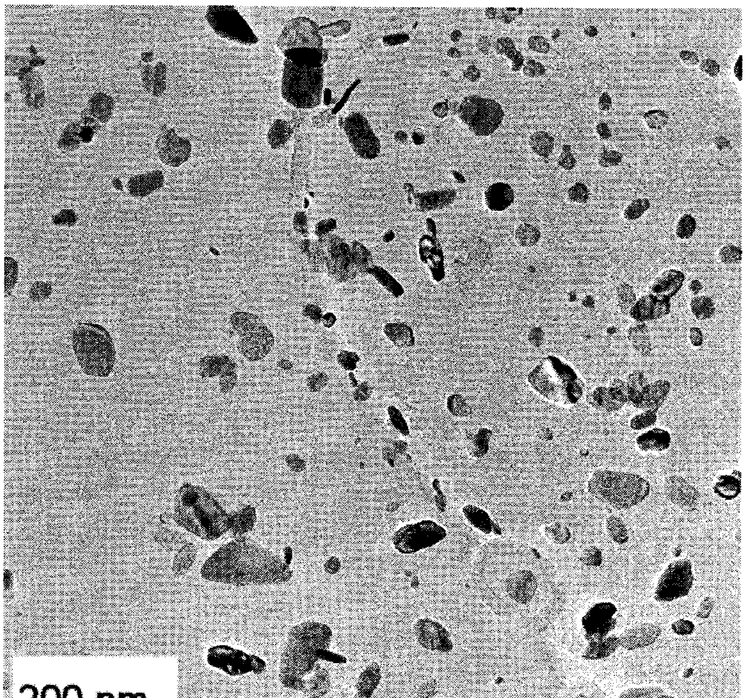

Fig. 4

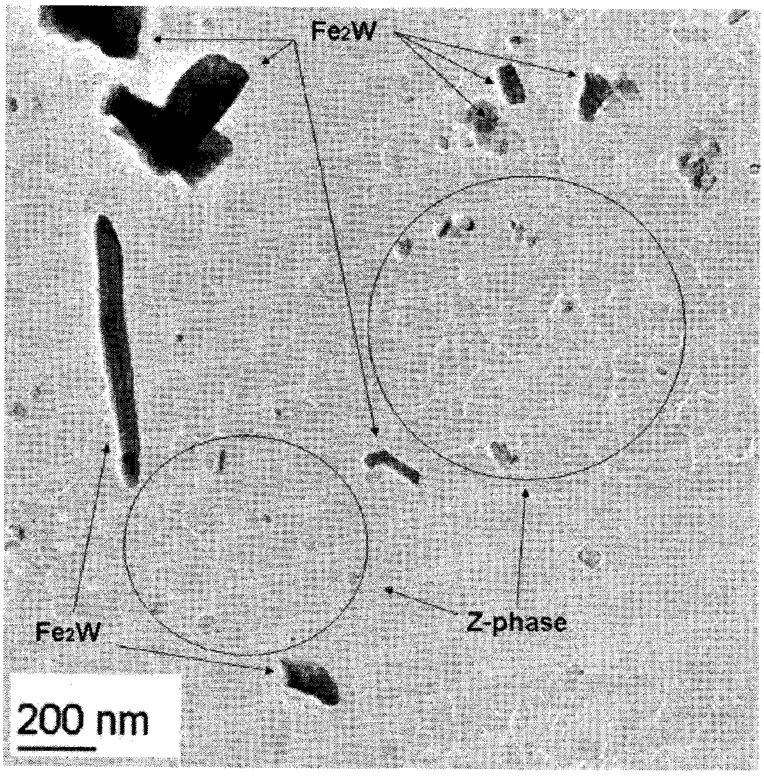

Fig. 5

# INTERNATIONAL SEARCH REPORT

International application No
PCT/DK2008/050049

## A. CLASSIFICATION OF SUBJECT MATTER

INV. C22C38/00

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)
C22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data, COMPENDEX, WPI Data, INSPEC

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | H.K. DANIELSEN, J.HALD: "Behaviour of Z phase in 9-12%Cr steels"<br>ENERGY MATERIALS,<br>vol. 1, no. 1, 2006, pages 49-57, XP002440821<br>cited in the application<br>page 51; examples P92,AXM,P122,T122,NF12; tables 1,2<br>page 54, right-hand column - page 55; figure 8<br>-----<br>-/-- | 1-6 |

☒ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

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"E" earlier document but published on or after the international filing date

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| | |
|---|---|
| Date of the actual completion of the international search<br>6 May 2008 | Date of mailing of the international search report<br>20/05/2008 |
| Name and mailing address of the ISA/<br>European Patent Office, P.B. 5818 Patentlaan 2<br>NL – 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,<br>Fax: (+31-70) 340-3016 | Authorized officer<br>Gavriliu, Alexandru |

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | R. AGAMENNONE, ET AL.: "Evolution of microstructure and deformation resistance in creep of tempered martensitic 9-12%Cr-2%W-5%Co steels"<br>ACTA MATERIALIA/ELSEVIER LTD., no. 54, 2006, pages 3003-3014, XP002440822<br>page 3004 - page 3005; tables 1,2<br>page 3008, left-hand column<br>abstract; figures 16,17 | 1-6 |
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