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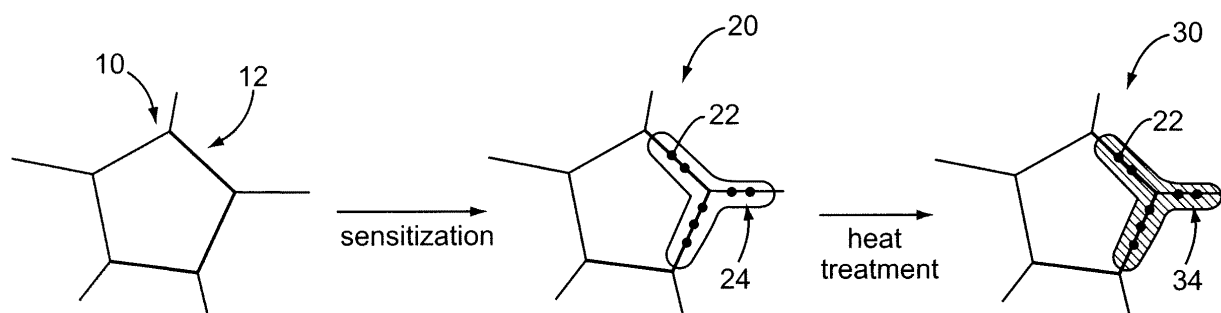
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(54) **Method of increasing resistance to stress corrosion cracking of austenitic stainless steels**

(57) A method of providing resistance to intergranular stress corrosion cracking in an alloy material, the method comprising sensitizing the alloy to form carbides

(22), allowing the carbides to precipitate, and applying a heat treatment to replenish a chromium-depleted zone (24).

FIG. 1



Description

[0001] The present disclosure is generally directed to methods for mitigation stress corrosion cracking in austenitic solid solution strengthened stainless steels.

[0002] In applications such as nuclear reactors, steam driven turbines, or water deaerators, high-temperatures in high purity water or water/steam systems can become aggressive environments that can adversely affect structural materials either by general corrosion or by stress corrosion cracking (SCC). For example, high temperature water may cause stress corrosion SCC in materials such as stainless steels, nickel-iron base alloys, and nickel base alloys. SCC develops when the material is subjected to an applied or residual tensile stress in the presence of some corrosive environment, especially chloride or sulfate-containing environments at higher temperatures. These stresses can result or originate from differences in thermal expansion or contraction between components, relatively high or varying operating pressures, or they can be residual stresses created by the various processes performed during the manufacture or assembly of the components or system. In addition to stresses, residual plastic strains produced during the manufacture or assembly of the components or system can make a material more susceptible to SCC. For example, SCC can result from residual stresses caused by welding, cold working, and other thermomechanical metal treatments. Stress corrosion cracking also includes cracks propagated by static or dynamic tensile stresses acting in combination with corrosion. Water chemistry, welding, heat treatment, and radiation may all increase the susceptibility of a metal or alloy component to stress corrosion cracking.

[0003] Intergranular stress corrosion cracking (IGSCC) is localized cracking that occurs at the grain boundaries of a susceptible material in an aggressive environment under load. Intergranular slip step oxidation reactions weaken the grain boundaries, which then open under an applied load and physical cracks are formed. The cracks propagate with little or no evidence of plastic deformation, and failure of the component is likely. Three simultaneous conditions are generally present for IGSCC to occur: localized changes to the material's chemical composition or grain boundary microstructure, residual or applied stresses, and exposure to a corrosive environment. All of these critical factors can contribute to the formation and propagation of a stress corrosion crack. For example, one common form of sensitization is caused by the thermal cycle of welding, where the post-weld cooling rate is sufficiently slow to allow precipitation of chromium-rich carbides at grain boundaries. The precipitation of carbides depletes the adjacent grain boundaries of chromium to an extent that they are no longer corrosion resistant. Hence, SCC can occur at these boundaries in otherwise corrosion-resistant materials when in the presence of a chemically aggressive water environment and a tensile stress.

[0004] IGSCC-related research has produced various mitigation methods that deal with each of these contributors. One method of mitigating stress corrosion cracking of susceptible material in, for example, a boiling water reactor is through the application of hydrogen water chemistry (HWC), which involves the addition of hydrogen gas to the reactor feedwater. Addition of hydrogen reduces the level of oxidizing species, such as dissolved oxygen and hydrogen peroxide, thereby reducing the stress corrosion cracking susceptibility. Unfortunately, the hydrogen water chemistry technique can require large quantities of hydrogen to effectively reduce the stress corrosion cracking susceptibility to acceptable levels in the various components.

[0005] Stainless steels, higher chromium super stainless steels, Fe-Ni-base and Ni-based alloys are alloyed with chromium to achieve general corrosion resistance but this approach can fail to mitigate SCC if the amount of Cr added is insufficient to maintain a stable oxide film in a corrosive environment or if microstructural changes create regions of lower chromium concentration. One problem is that these materials may not be microstructurally stable at their intended operating temperatures or may have been heat treated or welded to produce SCC susceptible microstructures. One approach employed to mitigate SCC is continual addition of oxide strengthening or stabilizing elements to a corrosive environment. Another approach utilizes the addition of catalytic elements (such as platinum) to generate hydrogen in a corrosive environment, the hydrogen reducing free oxygen in the water, thereby minimizing its corrosive inducing effects. One problem with this approach is that it requires a commitment by the end user to actively maintain the SCC mitigation strategy. Additionally, it will incur additional operating costs over a component or plant lifetime.

[0006] Therefore, there remains a need for new approaches to mitigate stress corrosion cracking.

[0007] Disclosed herein are methods for providing resistance to intergranular stress corrosion cracking in a Fe-Ni-Cr alloy material.

[0008] In one embodiment, the disclosure provides for a method for providing resistance to intergranular stress corrosion cracking in an Fe-Ni-Cr alloy material, the method comprising sensitizing the Fe-Ni-Cr alloy material to form carbide precipitates at grain boundary interfaces and chromium-depleted zones about the carbide precipitates, and heating the sensitized Fe-Ni-Cr alloy material to a temperature and a time effective to diffuse chromium into a chromium-depleted zone.

[0009] In another embodiment, the disclosure provides for a method for treating a sensitized Fe-Ni-Cr alloy material having carbide precipitates at grain boundary interfaces and a chromium-depleted zone about the carbide precipitates, the method comprising heating the sensitized Fe-Ni-Cr alloy material to a temperature and a time effective to diffuse chromium from a grain matrix of the Fe-Ni-Cr alloy material into the chromium-depleted zone, wherein resistance to the intergranular stress corrosion

cracking increases relative to the sensitized Fe-Ni-Cr in an absence of the heating.

[0010] Various features and advantages of the components and processes disclosed herein can be more readily understood by reference to the following drawings and detailed description, and the examples included therein, in which:

Figure 1 is a schematic illustration of a process for improving an alloy material's resistance to stress corrosion cracking.

Figure 2 illustrates the absence of chromium-rich carbides at grain boundaries in an 800H alloy after a solution anneal heat treatment.

Figure 3 illustrates chromium-rich carbide precipitated at the grain boundaries in an 800H alloy after a sensitization heat treatment.

[0011] The present disclosure generally relates to a method of mitigating stress corrosion cracking in austenitic solid solution strengthened stainless steels, specifically Fe-base, Fe-Ni base or Ni-base alloys, such as those used in high temperature and pressure aqueous environments. More particularly, it relates to preventing intergranular stress corrosion cracking (IGSCC) in austenitic solid solution strengthened 800 and 300 series of alloys. In contrast to the prior art, one disclosed method includes sensitizing the alloy component to form chromium carbide precipitates at the grain boundaries then extending the heat treatment time to allow diffusion of the chromium into the chromium depleted zones that resulted from sensitization. In the specific case of the 800 series of alloys the material may be left in a sensitized condition while in austenitic stainless steels the extended heat treatment will be required to recover the chromium composition at the grain boundaries. The chromium carbide precipitates, which are globular or lamellar in nature, in combination with the diffusion of chromium into the chromium-depleted zones provide enhanced resistance to IGSCC.

[0012] In another embodiment, an alloy component that has been sensitized can be exposed to a heat treatment process that causes diffusion of chromium into the chromium-depleted zones that resulted from sensitization. As noted above, the sensitized alloy component includes chromium-rich carbide precipitates at about the grain boundaries. In this manner, the alloy component undergoes a self-healing process.

[0013] As used herein, solution strengthened stainless steel is given its ordinary meaning and generally refers to a heat treatment process in which an alloy is heated to a suitable temperature, held at that temperature long enough to cause secondary phases to undergo solid state dissolve and result in one or more of the constituent elements of those phases to enter into the matrix phase solid solution, and then cooled rapidly enough to hold

these constituents in solution or to ensure that secondary phases do not re-precipitate. In this condition, microstructures are formed that are generally comprised of primary carbides dispersed in a single-phase matrix with essentially clean grain boundaries. In addition, the terms "first", "second", and the like do not denote any order or importance, but rather are used to distinguish one element from another, and the terms "the", "a", and "an" do not denote a limitation of quantity, but rather denote the presence of at least one of the referenced item. The modifier "about" used in connection with a quantity is inclusive of the stated value and has the meaning dictated by the context (e.g., includes the degree of error associated with measurement of the particular quantity). Furthermore, all ranges disclosed herein are inclusive of the endpoints and independently combinable.

[0014] In one embodiment, the process comprises sensitizing an alloy component followed by continued heating of the component after sensitization of an alloy material. As discussed above, sensitization can cause precipitation of chromium carbides at the grain boundaries. The precipitation of these carbides depletes the adjacent grain boundary regions of chromium to an extent that they are no longer corrosion resistant. Sensitization is caused by the formation of chromium carbides about the grain boundaries. The Cr-rich precipitate draws chromium from the adjacent matrix, which results in the formation of a chromium-depleted zone. If the chromium content is below 11-12 atomic percent in the chromium-depleted zone, the stainless steel is said to be sensitized.

[0015] As a result, the components would normally be susceptible to intergranular stress corrosion cracking (IGSCC). However, continued heating of the component having chromium-depleted zones at the grain boundaries is effective to diffuse chromium within the matrix into the chromium depleted zones. In one embodiment, the component having chromium-depleted zones is heated at about 450 to about 700°C for a period of time effective to cause chromium from the matrix to diffuse down the chromium composition gradient caused by sensitization and replenish the depleted zone along the boundary, restoring the metal's corrosion properties. The presence of intergranular chromium-rich carbides at the grain boundaries has been found, by the present disclosure, to provide enhanced resistance to IGSCC. More importantly, for some higher chromium Fe-Ni base alloys, such as the 800 series family of super stainless steels, the presence of chromium-rich carbides alone imparts an enhanced resistance to IGSCC growth. Thus, the present disclosure is generally directed to a heat treatment process designed to impart IGSCC resistance by first sensitizing the metal and then letting it self-heal. The resulting alloy material is IGSCC resistant to intergranular SCC promoting environments and under static or dynamic mechanical loading.

[0016] In an exemplary embodiment, the alloy material is an austenitic solid solution strengthened super stainless steel similar to the composition range of the 800

series of alloys. Austenitic stainless steels are generally characterized by high ductility, relatively low yield stress and ultimate tensile strengths, when in the annealed or solution annealed conditions, cold work will dramatically increase the tensile properties. A typical low carbon steel on cooling transforms from austenite to either a mixture of ferrite and iron carbide (Fe_3C). With austenitic stainless steel, the high chromium and nickel content suppress this transformation keeping the material essentially austenite on cooling.

[0017] Austenitic steels are classified in three groups, the AISA 200 series (alloys of iron-chromium-nickel-manganese), the AISA 300 series (alloys of iron-chromium-nickel), and nitrogen-strengthened alloys. The carbon content varies dependent on the series (generally 0.15% or less carbon) and in the 300 series is dependent on whether the alloy is an L-grade, low carbon concentration (0.03% or less), or of a nominal composition (0.08% or less). These alloy have a range of compositions but generally contain a minimum of 16% chromium with sufficient nickel and manganese to provide a stable austenitic structure at temperatures below the martensite start (Ms) temperature. Nitrogen-strengthened austenitic stainless steels are alloys of chromium-manganese-nitrogen; some grades also contain nickel. Austenitic stainless steels are generally used for corrosive or cryogenic environments where corrosion resistance and toughness are the primary requirements. Typical applications include shafts, pumps, fasteners, and piping in seawater and equipment for processing chemicals, food, and dairy products. Another classification, more relevant to this disclosure, is that of austenitic 'super stainless' steels that are mid-way between austenitic stainless steels and Fe-Ni base superalloys. These materials, represented by the alloy 800 series, are characterized by; much higher nickel and chromium contents, higher carbon levels, and intentional additions of small amounts of titanium and aluminum.

[0018] In an exemplary embodiment, the alloy material has a composition of 18-30% chromium, 8-80% nickel, and lesser alloying additions of carbon, nitrogen, molybdenum, niobium, titanium, and manganese.

[0019] Suitable austenitic alloys include, but are not meant to be limited to, the super stainless steels represented by the 800 series (19.0-23 wt% Cr, 30-35 wt% Ni, 0.15-0.6 wt% Al, 0.15-0.6 wt% Ti, and 10 wt% C max) and those of the 300 series such as stainless steel grade 304 (18-20% Cr and 8-12% Ni), 316 (16-18% Cr, 10-14% Ni, and 2-3% Mo), 316 Ti (316 with Titanium added), 320 (Same as 316 Ti), 321 (17-19%Cr, 9-12%Ni, and Titanium), 347 (17-19% Cr, 9-13% Ni, and Niobium), 308 (19-22% Cr, 9-11% Ni), 309 (22-24% Cr, 12-15% Ni), 310 (24-26% Cr, 19-22% Ni), 904L (20%Cr, 25%Ni, 4.5% Mo) and the like. Other alloying elements may include vanadium (V), aluminum (Al), tungsten (W), cobalt (Co), copper (Cu), nitrogen (N), and carbon (C). The number of grades is therefore seemingly infinite, with a large number of standard compositions to which manufactur-

ers add variants depending on the particular application. For the purposes of this disclosure, stainless steel grades with chromium concentrations below 16 wt% are not applicable, due to the fact that lower chromium concentrations will not provide adequate overall corrosion resistance for the intended applications due to the nature of a protective Cr oxide layer formed and the reduction of Cr in the alloy matrix due to the precipitation of Cr-rich intergranular carbides..

[0020] The alloys can be produced via various process paths such as for example casting, powder metallurgy or cast/wrought metallurgy. Alloy constituents can be melted using any conventional melt process such as air melting, Argon Oxygen Deoxidation (AOD), Ladle Refining, Vacuum Induction Melting (VIM), Vacuum Arc Re-Melting (VAR), Electro Slag Re-Melting (ESR), etc.

[0021] The alloy may then be homogenized prior to hot working or it may be heated and directly hot worked. If homogenization is used, it may be carried out by heating the alloy to a metal temperature in the range of about 1100°C to about 1400°C for a period of time of at least eight hours to dissolve soluble elements and carbides and to also homogenize the structure. A suitable time is eight hours or more in the homogenization metal temperature range. Normally, the soak time at the homogenization temperature does not have to extend for more than seventy-two hours. After homogenization, the alloy is typically hot worked. The alloy can be hot worked by, but not limited to: hot rolling, hot forging, or hot extrusion or any combinations thereof to yield the desired size and shape. This process is followed by delivery of the alloy product to a customer for final manufacture of a component part and appropriate heat treating and finishing. Typically the customer will form the alloy into a desired shape. Heat treatment, warm work, or cold work separately or in various combinations may be employed to obtain the tensile properties and fracture toughness desired.

[0022] Figure 1 schematically illustrates the grain boundaries in an austenitic super stainless steel in the solution annealed condition. In step 10, prior to the sensitization and heat treatment process of the disclosure, the interfaces 12 of several grains of a polycrystalline alloy material are shown that exhibit essentially clean grain boundaries, wherein chromium carbide precipitation has not yet occurred. In step 20, the steel alloy material is first exposed to a sensitization process, wherein the steel alloy material has been heated and cooled at rates and conditions such that chromium carbide precipitates 22 are formed at the grain boundary interfaces. The formation of the chromium carbide precipitates results in a chromium-depleted zone 24 about the chromium carbide precipitates. In an exemplary embodiment, the chromium carbide precipitate 22 is Cr_{23}C_6 and may further include, Mo, V, W, Nb, Ta, B, and combinations thereof. Dependent on the alloy in question in step 30, the steel alloy may next be subjected to a heat treatment process that permits chromium diffusion into the chromium-depleted zone 24. The heat treatment process may

be independently performed or may be integrated with a process that results in sensitization, i.e., formation of chromium carbides at the grain boundary interfaces. Subsequent thermal exposure; heat treatment, operation, or processing of the component drives the diffusion of chromium down the Cr composition gradient generated by the precipitation and growth of chromium carbides and restores the material's corrosion resistance properties. The presence of intergranular carbides with the diffused chromium at the interfaces provides resistance to intergranular stress corrosion cracking.

[0023] The heating source can be any method capable of replenishing the chromium-depleted zone as described above. In one embodiment, the heating source can be a gas or electric furnace, inductive, infrared, molten salt or metal baths, or laser. In another embodiment the heat source can be localized to specific areas of a component using the methods described above or may occur as a consequence of manufacturing, welding or heat treatment or during component operation in an elevated temperature environment.

[0024] The use of extended time heat treatments to achieve IGSCC resistant grain boundary chemistries that are corrosion resistant provides an economical path to preventing IGSCC. Heat treatment is a relatively inexpensive process compared with specifying a specialty-grade alloy or with a post-assembly heat treatment. This disclosure will provide a significant material and labor cost savings while providing superior lifetimes on gasification products. In addition, the disclosed heat treatment process will be of benefit, for example, to any business that requires IGSCC resistance of austenitic alloys used in structural components for gasification, nuclear, water, and oil and gas industries, among others.

[0025] The following examples fall within the scope of, and serve to exemplify, the more generally described methods set forth above. The examples are presented for illustrative purposes only, and are not intended to limit the scope of the disclosure.

Example 1

[0026] In one example, sensitization properties of alloy 800H were studied. IGSCC tests on sensitized samples confirmed IGSCC resistance. Duplicate testing was performed on alloy 800H comprising sensitization, carbide precipitation, and subsequent heat treatment according to the process of this disclosure. Sensitization was detected using ASTM A262 Practice C boiling nitric acid (or 'Huey') test and confirmed by measuring the chromium concentration of the regions adjacent to the grain boundaries using a Transmission Electron Microscope (TEM). In more conclusive proof of the efficacy of this disclosure the IGSCC growth rate was measured in a high temperature (288°C) and pressure (1500 psig) aqueous environment in alloy 800H heat treated to precipitate intergranular $M_{23}C_6$ carbides. The mechanical test conditions used for the test were designed to induce IGSCC in

austenitic metals over a wide range in chemical compositions. Test results from the sensitization heat treated material showed extremely low IGSCC growth rates (1×10^{-9} mm/s) that indicate a very low probability for sustained SCC growth. This is in comparison with IGSCC growth rate of above 1×10^{-7} mm/s for typical sensitized materials tested under similar conditions.

[0027] This written description uses examples to disclose the preferred mode, and also to enable any person skilled in the art to practice the invention, including making and using any devices or systems and performing any incorporated methods. The patentable scope of the invention is defined by the claims, and may include other examples that occur to those skilled in the art. Such other examples are intended to be within the scope of the claims if they have structural elements that do not differ from the literal language of the claims, or if they include equivalent structural elements with insubstantial differences from the literal languages of the claims.

[0028] Various aspects and embodiments of the present invention are now defined by the following numbered clauses:

1. A method for providing resistance to intergranular stress corrosion cracking in an Fe-Ni-Cr alloy material, the method comprising:

sensitizing the Fe-Ni-Cr alloy material to form carbide precipitates at grain boundary interfaces and chromium-depleted zones about the carbide precipitates; and

heating the sensitized Fe-Ni-Cr alloy material to a temperature and a time effective to diffuse chromium into a chromium-depleted zone.

2. The method of clause 1, wherein the Fe-Ni-Cr alloy material comprises at least 16% chromium.

3. The method of any preceding clause, wherein sensitizing and heating the Fe-Ni-Cr alloy material is at a temperature from about 450°C to 700°C.

4. The method of any preceding clause, wherein sensitizing the Fe-Ni-Cr alloy material comprises a welding process.

5. The method of any preceding clause, wherein the carbide precipitates comprise chromium.

6. The method of any preceding clause, wherein the carbide precipitates are of the formula $Cr_{23}C_6$, Cr_7C_3 and combinations thereof.

7. The method of any preceding clause, wherein the carbide precipitates further comprise Fe, Mo, V, W, Ti, Nb, Ta, Hf, and combinations thereof.

8. A method for treating a sensitized Fe-Ni-Cr alloy material having carbide precipitates at grain boundary interfaces and a chromium-depleted zone about the carbide precipitates, the method comprising:

heating the sensitized Fe-Ni-Cr alloy material to a temperature and a time effective to diffuse chromium from a grain matrix of the Fe-Ni-Cr alloy material into the chromium-depleted zone, wherein resistance to the intergranular stress corrosion cracking increases relative to the sensitized Fe-Ni-Cr in an absence of the heating.

9. The method of clause 8, wherein the Fe-Ni-Cr alloy material comprises at least 16% chromium.

10. The method of clause 8 or 9, wherein heating the Fe-Ni-Cr alloy material is at a temperature from about 450°C to 700°C.

11. The method of any of clauses 8 to 10, wherein heating is for a period of time in a range of about 10 to about 3000 hours.

12. The method of any of clauses 8 to 11, wherein the carbide precipitates comprise chromium.

13. The method of any of clauses 8 to 12, wherein the carbide precipitates are of the formula Cr_{23}C_6 , Cr_7C_3 and combinations thereof.

14. The method of any of clauses 8 to 13, wherein the carbide precipitates further comprise Fe, Ti, Mo, V, W, Nb, Ta, Hf, and combinations thereof.

4. The method of any one of the preceding claims, wherein the carbide precipitates are of the formula Cr_{23}C_6 , Cr_7C_3 and combinations thereof.

5. The method of any one of the preceding claims, wherein the carbide precipitates further comprise Fe, Mo, V, W, Ti, Nb, Ta, Hf, and combinations thereof.

6. A method for treating a sensitized Fe-Ni-Cr alloy material having carbide precipitates at grain boundary interfaces (12) and a chromium-depleted zone (24) about the carbide precipitates (22), the method comprising: heating the sensitized Fe-Ni-Cr alloy material to a temperature and a time effective to diffuse chromium (34) from a grain matrix of the Fe-Ni-Cr alloy material into the chromium-depleted zone (24), wherein resistance to the intergranular stress corrosion cracking increases relative to the sensitized Fe-Ni-Cr in an absence of the heating.

7. The method of claim 6, wherein the Fe-Ni-Cr alloy material comprises at least 16% chromium.

8. The method of any of preceding claims 6 and 7, wherein the carbide precipitates comprise chromium.

9. The method of any of preceding claims 6-8, wherein the carbide precipitates are of the formula Cr_{23}C_6 , Cr_7C_3 and combinations thereof.

10. The method of any of preceding claims 6-9, wherein the carbide precipitates further comprise Fe, Ti, Mo, V, W, Nb, Ta, Hf, and combinations thereof.

Claims

1. A method for providing resistance to intergranular stress corrosion cracking in an Fe-Ni-Cr alloy material, the method comprising:

sensitizing the Fe-Ni-Cr alloy material to form carbide precipitates (22) at grain boundary interfaces (12) and chromium-depleted zones (24) about the carbide precipitates (22); and heating the sensitized Fe-Ni-Cr alloy material to a temperature and a time effective to diffuse chromium (34) into a chromium-depleted zone (24).

2. The method of claim 1, wherein the Fe-Ni-Cr alloy material comprises at least 16% chromium.

3. The method of any one of the preceding claims, wherein the carbide precipitates comprise chromium.

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FIG. 1

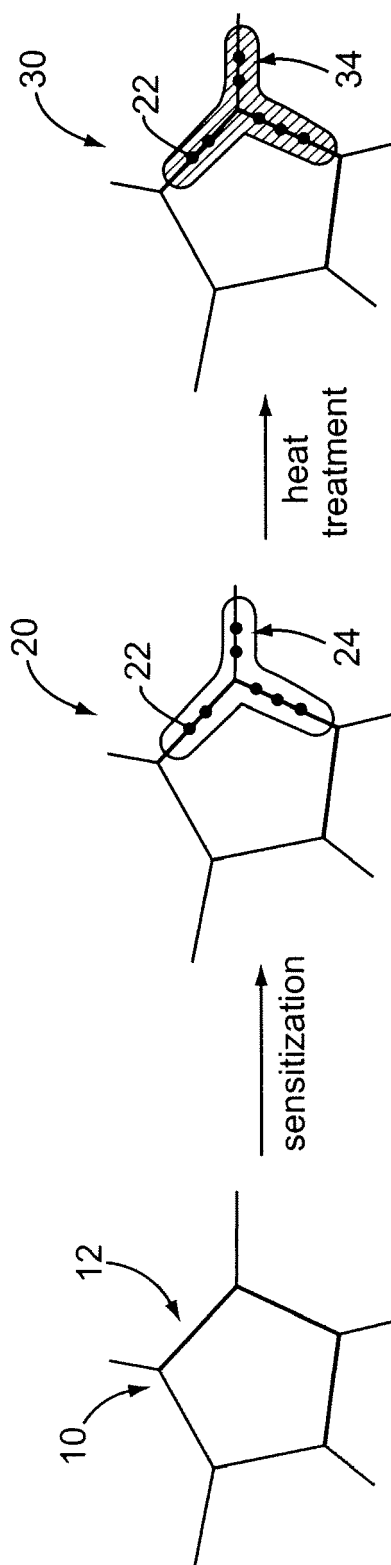


FIG. 2

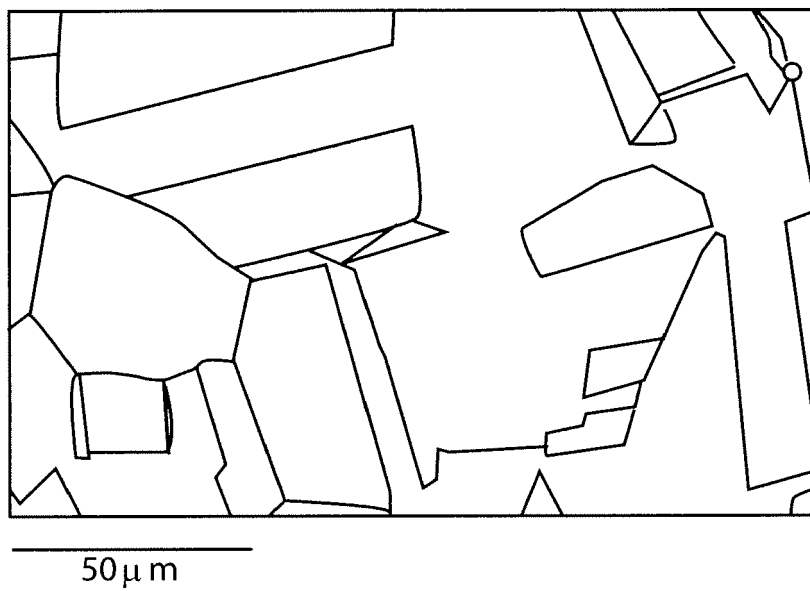
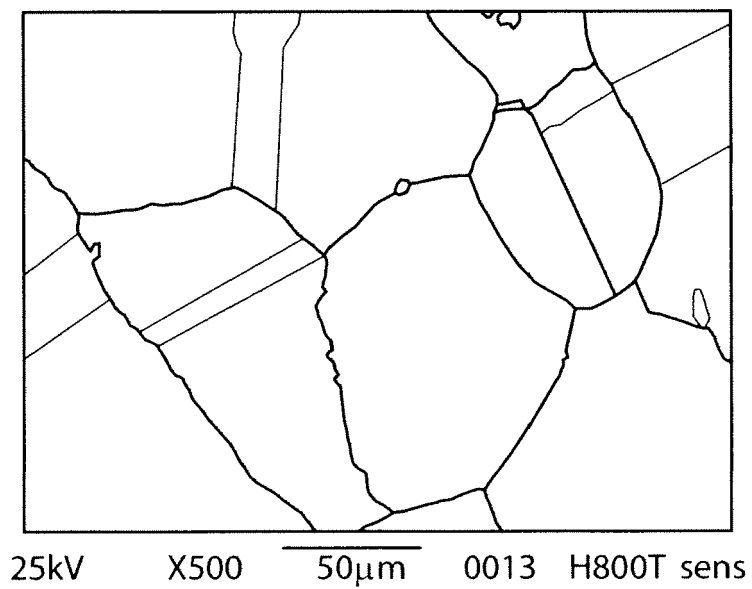


FIG. 3



**PARTIAL EUROPEAN SEARCH REPORT**

Application Number

which under Rule 63 of the European Patent Convention EP 09 15 4817 shall be considered, for the purposes of subsequent proceedings, as the European search report

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 4 168 994 A (OWENS CLARK M) 25 September 1979 (1979-09-25) * the whole document *	1-10	INV. C21D6/02 C21D6/00 C21D1/00
X	----- STEFEC, RUDOLF: "Structure corrosion of alloyed austenite" KORROSION (DRESDEN) , 11(6), 303-10 CODEN: KRRSAU; ISSN: 0368-6752, 1980, XP009119269 * the whole document *	1-10	
X	----- JP 60 197816 A (MITSUBISHI HEAVY IND LTD) 7 October 1985 (1985-10-07) * abstract *	1-10	
X	----- DEVINE ET AL: "Kinetics of sensitization and de-sensitization of duplex 308 stainless steel" ACTA METALLURGICA, PERGAMON PRESS, US, vol. 36, no. 6, 1 June 1988 (1988-06-01), pages 1491-1501, XP024024733 ISSN: 0001-6160 [retrieved on 1988-06-01] * the whole document *	1-10	
			TECHNICAL FIELDS SEARCHED (IPC)
			C21D
INCOMPLETE SEARCH The Search Division considers that the present application, or one or more of its claims, does/do not comply with the EPC to such an extent that a meaningful search into the state of the art cannot be carried out, or can only be carried out partially, for these claims. Claims searched completely : Claims searched incompletely : Claims not searched : Reason for the limitation of the search: see sheet C			
Place of search		Date of completion of the search	Examiner
Munich		3 July 2009	Patton, Guy
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			

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PARTIAL EUROPEAN SEARCH REPORT

Application Number

EP 09 15 4817

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (IPC)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	DATABASE CA [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; 22 April 2001 (2001-04-22), BROWN, HIRAM: "Carbides in 310 stainless steel" XP002535099 retrieved from STN Database accession no. 1954:56254 * abstract * -& BROWN, HIRAM: "Carbides in 310 stainless steel" STEEL (CLEVELAND) , 135(NO. 3;NO. 4), 106-8;92-4 CODEN: STELAC, 1954, XP009119349 -----	1-10	
X	JP 54 069516 A (HITACHI LTD) 4 June 1979 (1979-06-04) * abstract *	1-10	TECHNICAL FIELDS SEARCHED (IPC)
X	WHITE, WILLIAM E. ET AL: "Metallographic observations on the formation and occurrence of ferrite, sigma phase, and carbides in austenitic stainless steels. I. AISI type 310 stainless steel" METALLOGRAPHY , 3(1), 35-50 CODEN: MEIJAP; ISSN: 0026-0800, 1970, XP023901147 * the whole document *	1-10	
X	WHITE, WILLIAM E. ET AL: "Metallographic observations on the formation and occurrence of ferrite, sigma phase, and carbides in austenitic stainless steels. II. AISI type 316 stainless steel" METALLOGRAPHY , 3(1), 51-60 CODEN: MEIJAP; ISSN: 0026-0800, 1970, XP024083071 * the whole document * ----- -/--	1-10	



PARTIAL EUROPEAN SEARCH REPORT

Application Number
EP 09 15 4817

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (IPC)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	WHITE, W. E. ET AL: "Metallographic observations on the formation and occurrence of ferrite, sigma phase, and carbides in austenitic stainless steels. III. Electron microscopy studies" METALLOGRAPHY , 5(4), 333-45 CODEN: MEIJAP; ISSN: 0026-0800, 1972, XP024354896 * the whole document * -----	1-10	
			TECHNICAL FIELDS SEARCHED (IPC)



**INCOMPLETE SEARCH
SHEET C**

Application Number

EP 09 15 4817

Claim(s) not searched:

-

Reason for the limitation of the search:

The initial phase of the search revealed a very large number of documents relevant to the issue of novelty. So many documents were retrieved that it is impossible to determine which parts of the claims 1-10 may be said to define subject-matter for which protection might legitimately be sought (Art. 84 EPC).

For instance, reference is made to the following documents cited in the search report:

D1: US-A-4 168 994 (OWENS CLARK M) 25 September 1979

D2: STEFEC, RUDOLF: "Structure corrosion of alloyed austenite" KORROSION (DRESDEN) , 11(6), 303-10 CODEN: KRRSAU; ISSN: 0368-6752, 1980, XP009119269

D3: JP 60 197816 A (MITSUBISHI HEAVY IND LTD) 7 October 1985

D4: DEVINE ET AL: "Kinetics of sensitization and de-sensitization of duplex 308 stainless steel" ACTA METALLURGICA, PERGAMON PRESS, US, vol. 36, no. 6, 1 June 1988 (1988-06-01), pages 1491-1501, XP024024733 ISSN: 0001-6160 [retrieved on 1988-06-01]

D5: DATABASE CA [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; 22 April 2001 (2001-04-22), BROWN, HIRAM: "Carbides in 310 stainless steel" XP002535099 retrieved from STN Database accession no. 1954:56254

D6: JP 54 069516 A (HITACHI LTD) 4 June 1979

D7: WHITE, WILLIAM E. ET AL: "Metallographic observations on the formation and occurrence of ferrite, sigma phase, and carbides in austenitic stainless steels. I. AISI type 310 stainless steel" METALLOGRAPHY , 3(1), 35-50 CODEN: MEIJAP; ISSN: 0026-0800, 1970, XP023901147

D8: WHITE, WILLIAM E. ET AL: "Metallographic observations on the formation and occurrence of ferrite, sigma phase, and carbides in austenitic stainless steels. II. AISI type 316 stainless steel" METALLOGRAPHY , 3(1), 51-60 CODEN: MEIJAP; ISSN: 0026-0800, 1970, XP024083071

D9: WHITE, W. E. ET AL: "Metallographic observations on the formation and occurrence of ferrite, sigma phase, and carbides in austenitic stainless steels. III. Electron microscopy studies" METALLOGRAPHY , 5(4), 333-45 CODEN: MEIJAP; ISSN: 0026-0800, 1972, XP024354896

D1 discloses a method for providing resistance to intergranular stress corrosion cracking in an Fe-Ni-Cr alloy material, the method comprising:
a) - sensitizing the Fe-Ni-Cr alloy material to form carbide precipitates at grain boundary interfaces and chromium-depleted zones about the carbide precipitates; and
b) - heating the sensitized Fe-Ni-Cr alloy material to a temperature and a time effective to diffuse chromium into a chromium-depleted zone (see for instance D1, col. 1, l. 6-26; col. 1, l. 55-65; col. 2, l. 13-42; claims).

As a result, all features of claim 1 are known from D1 and, hence, its subject-matter is not novel over D1 (Art. 52(1), 54(1) EPC).

Like D1, each document D2-D9 discloses all features of claim 1 (D2, "1. Einleitung", p. 303-304; "2.4. Karbidausscheidung", p. 308-309) (D3,



**INCOMPLETE SEARCH
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abstract) (D4, "Summary", p. 1500-1501) (D5, STN abstract; "Theory", p. 93-94) (D6, abstract) (D7, p. 48-49; "Summary", p. 49-50) (D8, p. 59-60; "Summary", p. 60) (D9, "General Observations", p. 334-335; p. 339; "Summary", p. 344-345). As a result, the subject-matter of claim 1 is not novel over each document D2-D9 (Art. 52(1), 54(1) EPC).

Independent claim 6 does not contain any additional feature compared to claim 1. Therefore, above objections also apply against claim 6 (Art. 52(1), 54(1) EPC).

In addition, the additional features of claims 2-5, 7-10 are known from at least one of the documents D1-D9 (Art. 52(1), 54(1) EPC).

For these reasons, a meaningful search of the whole claimed subject matter of claims 1-10 could not be carried out (Rule 63 EPC).

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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03-07-2009

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4168994	A	25-09-1979	BR 7907331 A	08-07-1980
			CA 1130704 A1	31-08-1982
			DE 2963433 D1	16-09-1982
			EP 0011152 A1	28-05-1980
			ES 485891 A1	16-05-1980
			JP 55069221 A	24-05-1980

JP 60197816	A	07-10-1985	NONE	

JP 54069516	A	04-06-1979	NONE	

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82