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(54) **AUSTENITIC STAINLESS STEEL ALLOY**

(57) An austenitic stainless steel alloy is provided that includes 0.7-1.2 wt % ofN, 10-25 wt % of Ni, 26-34 wt % of Cr, 0.1-1.0 wt % ofNb, 0.1-1.0 wt % of V, and a balance of Fe and incidental impurities.

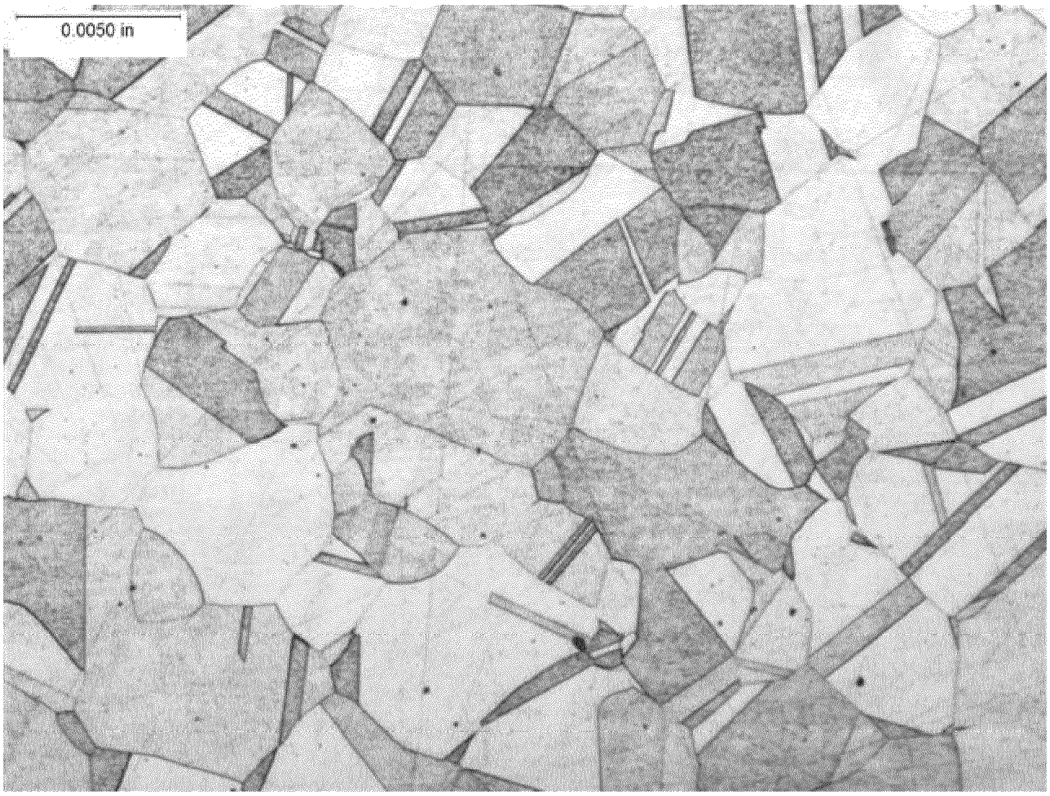

Figure 1

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Description

FIELD TO THE INVENTION

[0001] This invention relates generally to an alloy and, in particular, to an austenitic stainless steel alloy having very high annealed strength in combination with good corrosion resistance, and capable of being hot worked from cast ingots.

BACKGROUND

[0002] Nitrogen (N) containing austenitic stainless steels are known for their high annealed yield strength, and corrosion properties. However, known nitrogen-containing austenitic stainless steels do not have the annealed yield strength and corrosion resistance needed in many oil-field applications. Furthermore, severe tearing occurs during hot working of a conventional cast ingot of known austenitic stainless steel, especially in very high chromium (Cr) and N alloys.

[0003] In view of these foregoing comments, a need has arisen for an austenitic stainless steel with a combination of a unique annealed yield strength of 95ksi minimum with excellent corrosion resistance that is capable of being hot worked without severe tears using conventional cast, including electroslag remelted, ingots.

SUMMARY OF THE INVENTION

[0004] It is therefore an object of the invention, among others, to provide a very high annealed strength, high toughness austenitic stainless steel alloy

[0005] This object is met by claim 1. Preferred embodiments are disclosed in the subclaims.

[0006] The inventive very high annealed strength, high toughness austenitic stainless steel alloy includes 0.7-1.2 wt % ofN, 10-25 wt % ofNi, 26-34 wt % ofCr, 0.1-1.0 wt % ofNb, 0.1-1.0 wt % of V, and a balance of Fe and incidental impurities.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] The invention will now be described by way of example with reference to the accompanying figures, of which:

Figure 1 is a micrograph showing an austenitic stainless steel alloy prepared according to example 1;
Figure 2 is a micrograph showing an austenitic stainless steel alloy prepared according to example 2; and
Figure 3 is a micrograph showing an austenitic stainless steel alloy prepared according to example 3;

DETAILED DESCRIPTION OF THE EMBODIMENT(S)

[0008] The invention is an austenitic stainless steel alloy having high amounts of Cr and N, as well as an addition of nickel (Ni), niobium (Nb) and vanadium (V), to improve desirable material properties, such as corrosion resistance, annealed yield strength, and tearing resistance.

[0009] The austenitic stainless steel alloy according to the invention includes a base composition of N, Cr, Ni, Nb, V, as well as carbon (C), molybdenum (Mo), copper (Cu), manganese (Mn), sulfur (S), silicon (Si), boron (B), and a base metal of iron (Fe). In particular, in an exemplary embodiment of the invention, the austenitic stainless steel alloy includes a nominal composition having a proportion of.7 to 1.2 wt% ofN, 26 to 34 wt% of Cr, 10 to 25 wt% of Ni, 0.1 to 1.0 wt% Nb, 0.1 to 1.0 wt% of V, and a balance wt % of Fe to complete the composition.

[0010] In another exemplary embodiment of the invention, the austenitic stainless steel alloy may include a composition having other elements and impurities with a proportion of ≤ .08 wt % of C, ≤ 4.0 wt% of Mo, ≤ 4 wt% of Cu, 2.0 to 10.0 wt% of Mn, ≤ .01 wt% of S, ≤ 2 wt% of Si, ≤ .006 wt% of B, as shown in Table 1.

TABLE 1

Exemplary Austenitic Stainless Steel Alloy Compositions			
Element	**Comp. A (wt %)**	**Comp. B (wt %)**	**Comp. C (wt %)**
C	≤ .08%	≤ .05%	≤ .03%
N	.7 to 1.2%	.75 to 1.10%	.8 to 1.0%
Cr	26 to 34%	28 to 33%	30 to 32%
Ni	10 to 25%	12 to 22%	14 to 18%

(continued)

Exemplary Austenitic Stainless Steel Alloy Compositions			
Element	**Comp. A (wt %)**	**Comp. B (wt %)**	**Comp. C (wt %)**
Mo	≤ 4.0%	0.5 to 3.0%	0.75 to 1.50%
Nb	0.1 to 1.0%	0.1 to 0.5%	0.1 to 0.3%
V	0.1 to 1.0%	0.1 to 0.5%	0.1 to 0.3%
Cu	≤ 4%	<3%	0.5 to 2.5%
Mn	2.0 to 10.0%	3.0 to 8.0%	4.0 to 7.0%
S	≤ .01%	≤ .005%	≤ .003%
Si	≤ 2%	≤ 1%	≤ 1%
B	≤ .006%	.001-.005%	.002-.004%

[0011] In an exemplary embodiment of the invention, the austenitic stainless steel alloy composition may includes about ≤ .08 wt % C. Carbon is a strong austenite-forming element which prevents ferrite and intermetallic phases. It contributes to high strength and toughness; however, , too much carbon will results in carbides which degrade corrosion resistance. As a result, lower carbon content may be used for intergranular corrosion resistance.

[0012] In another exemplary embodiment of the invention, the austenitic stainless steel alloy composition includes ≤ .05 wt % C. In yet another exemplary embodiment of the invention, the austenitic stainless steel alloy composition includes ≤ .03 wt % C.

[0013] The austenitic stainless steel alloy composition according to the invention may also include about 0.7 to about 1.2 wt % N. While the presence of N is used to achieve the austenite structure, strength, and chloride corrosion resistance, excessive nitrogen can form stable chromium nitrides that would degrade mechanical and corrosion properties. Accordingly, the N content is limited to 1.2%.

[0014] In another exemplary embodiment of the invention, the austenitic stainless steel alloy composition may include about 0.75 to about 1.10 wt % N. In yet another exemplary embodiment of the invention, the austenitic stainless steel alloy composition may include about 0.8 to about 1.0 wt % N.

[0015] The austenitic stainless steel alloy composition according to the invention further includes about 26 to about 34 wt % Cr. Cr increases the chloride corrosion resistance and nitrogen solubility of the composition. Too much Cr can result in stable intermetallic phases causing a negative effect on corrosion, toughness, and hot workability.

[0016] In another exemplary embodiment of the invention , the austenitic stainless steel alloy composition may include about 28 to about 33 wt % Cr. In yet another exemplary embodiment of the invention , the austenitic stainless steel alloy composition may include about 30 to about 32 wt % Cr.

[0017] The austenitic stainless steel alloy composition according to the invention further includes about 10 to about 25 wt % Ni. While Ni increases the toughness of the composition and, is a key austenite forming element in a high Cr alloy, too much Ni can negatively affect nitrogen solubility and hot workability. In another exemplary embodiment of the invention, the austenitic stainless steel alloy composition may include about 12 to about 22 wt % Ni. In yet another exemplary embodiment of the invention, the austenitic stainless steel alloy composition may include about 14 to about 18 wt % Ni.

[0018] The austenitic stainless steel alloy composition according to the invention includes about ≤ 4.0 wt % Mo. While Mo provides chloride and hydrogen sulfide corrosion resistance, the presence of Mo can form deleterious intermetallics phases which can affect corrosion, mechanical properties, and hot workability. Accordingly, the Mo content is kept lower. In another exemplary embodiment of the invention, the austenitic stainless steel alloy composition may include about 0.5 to about 3.0 wt % Mo. In another exemplary embodiment of the invention, the austenitic stainless steel alloy composition may include about 0.75 to about 1.50 wt % Mo.

[0019] The austenitic stainless steel alloy composition according to the invention further includes about 0.1 to about 1.0 wt % Nb. Niobium improves grain refining, retardation of grain growth , and strengthening of the austenitic stainless steel alloy. Too much niobium may degrade toughness and corrosion resistance by the formation of primary carbides or nitrides. In another exemplary embodiment of the invention, the austenitic stainless steel alloy composition may include about 0.1 to about 0.5 wt % Nb. In yet another exemplary embodiment of the invention, the austenitic stainless steel alloy composition may include about 0.1 to about 0.3 wt % Nb. One skilled in art should appreciate that Nb can be interchanged with columbium(Cb), as well as the aforementioned compositions, since it is recognized that both are the same element.

[0020] The austenitic stainless steel alloy composition according to the invention further includes about 0.1 to about 1.0 wt % V. Vanadium may be a carbide and nitride former that contributes to the high strength and toughness of the composition, by promoting grain refinement.. Too much vanadium may degrade corrosion and toughness by the formation of primary carbides or nitrides. In another exemplary embodiment of the invention, the austenitic stainless steel alloy composition may include about 0.1 to about 0.5 wt % V. In yet another exemplary embodiment of the invention, the austenitic stainless steel alloy composition may include about 0.1 to about 0.3 wt % V.

[0021] The austenitic stainless steel alloy composition also includes ≤ 4 wt % Cu. While Cu enhances austenite formation and improves corrosion resistance, too much Cu can result in poor hot workability. In another exemplary embodiment of the invention, the austenitic stainless steel alloy composition may include ≤ 3 wt % Cu. In yet another exemplary embodiment of the invention, the austenitic stainless steel alloy composition includes about 0.5 to about 7.0 wt % Cu.

[0022] The austenitic stainless steel alloy composition also includes about 2.0 to about 10.0 wt % Mn. Nitrogen solubility, necessary in this alloy, is increased by Mn ;. however, too much Mn can degrade corrosion resistance. In another exemplary embodiment of the invention, the austenitic stainless steel alloy composition may include about 3.0 to about 8.0 wt % Mn. In yet another exemplary embodiment of the invention, the austenitic stainless steel alloy composition includes about 4.0 to about 7.0 wt % Mn..

[0023] The austenitic stainless steel alloy composition may include ≤ .01 wt % S from scrap charge, but is restricted to enhance hot workability and corrosion resistance. In another exemplary embodiment of the invention, the austenitic stainless steel alloy composition may include ≤ .005 wt % S. In yet another exemplary embodiment of the invention, the austenitic stainless steel alloy composition includes ≤ .003 wt % S.

[0024] The austenitic stainless steel alloy composition also includes ≤ 2 wt % Si. Si may be is added for deoxidation, since low oxygen improves hot workability.. In another exemplary embodiment of the invention, the austenitic stainless steel alloy composition may include ≤ 1 wt % Si.

[0025] The austenitic stainless steel alloy composition also includes ≤ .006 wt % B. B may be added to improve hot workability in fully austenitic stainless steels. In another exemplary embodiment of the invention, the austenitic stainless steel alloy composition may include about .001 to about .005 wt % B. In yet another exemplary embodiment of the invention, the austenitic stainless steel alloy composition includes .002 to about .004 wt % B.

[0026] The balance of the austenitic stainless steel alloy composition according to the invention is substantially Fe.

[0027] In an exemplary embodiment of the invention, the austenitic stainless steel alloy composition may also include additional elements and known impurities common in commercial grades of similar compositions. One of ordinary skill in the art would also appreciate that other impurities may also be present in trace amounts.

TABLE 2

Exemplary Austenitic Stainless Steel Alloy Compositions with and without Nb and V			
Element	Example 1 wt. %	Example 2 wt. %	Example 3 wt. %
Carbon	0.026	0.021	0.022
Manganese	5.96	6.02	5.97
Silicon	0.19	0.13	0.15
Sulfur	<0.0005	<0.0005	<.0005
Chromium	30.89	31.10	30.92
Nickel	15.33	15.31	13.35
Molybdenum	1.01	1.01	1.01
Copper	0.16	0.16	2.65
Boron	0.0018	0.0017	0.0018
Nitrogen	0.84	0.91	0.92
Oxygen	0.0043	0.0016	0.0014
Niobium	<0.01	0.19	0.19
Vanadium	<0.01	0.20	0.20
Iron	Balance	Balance	Balance

[0028] As shown in Table 2, the austenitic stainless steel alloy according to invention was prepared using three separate heats (Examples 1-3). In Example 1, the austenitic stainless steel alloy composition was prepared with minimal amounts ofNb and V, while Examples 2 and 3 include approximately .2 wt % of Nb and .2 wt % of V to provide greater yield and ultimate tensile strength, an increase in hardness with an increase in grain size number, i.e. finer grain size Corrosion resistance in hydrogen sulfide (H_2S) and chloride (Cl) environments are similar for all three examples.

TABLE 3

Material Properties of the Exemplary Austenitic Stainless Steel Alloy Compositions with and without Nb and V									
Ex.	Condition	%Nb/V	%Cu	YS (ksi)	UTS (ksi)	%El	%RA	Hardness (HRC)	Grain Size No.
1	Press Forged Annealed	None	None	76.0	140.0	69.0	80.0	24.3	5
1	Hot Rolled Annealed	None	None	72.5	137.0	69.0	79.0	24.5	4/5
2	Press Forged Annealed	0.2/0.2	None	113.5	171.0	48.0	63.0	35.5	7/8
2	Hot Rolled Annealed	0.2/0.2	None	103.0	166.0	51.0	67.0	32.9	7
3	Press Forged Annealed	0.2/0.2	2.5	105.0	164.5	50.0	64.0	36.8	7/8
3	Hot Rolled Annealed	0.2/0.2	2.5	104.5	164.0	52.0	65.0	34.1	7

[0029] As shown in Table 3, material properties of the austenitic stainless steel alloys according to invention were prepared with three separate heats (Examples 1-3). In Example 1, the austenitic stainless steel alloy composition was prepared with minimal amounts of Nb and V. Material properties of Example 1 were observed after Example 1 was annealed, and either press forged or hot rolled. Examples 2 and 3, having approximately 0.2 wt % ofNb and 0.2 wt % of V, were also annealed and either press forged or hot rolled. The material properties of Examples 2 and 3 were also observed after being annealed, and either press forged or hot rolled and listed in Table 3. As shown, the addition of Nb and V into the austenitic stainless steel alloy provides increased yield strength (YS), ultimate tensile strength (UTS), increased hardness (HRC), and grain size number, i.e. finer grain size. The decreased elongation (El) and reduction in area (RA) is not considered significant. Besides properties listed in Table 3, crevice corrosion tests in 6%FeCl3 @40C for 72hrs showed that all examples had no weight loss. These data demonstrate the alloys' good chloride corrosion resistance. Also, no degradation in tensile ductility, both reduction of area and elongation, was determined when all examples were tested in an autoclave in a 0.3psi H2S, 200psi CO2, 20%NaCl, 5.5pH, 350F environment.

[0030] Figure 1 shows a micrograph of the austenitic stainless steel alloy composition of Example 1, where the composition has no amount ofNb and V. The grain size of the austenitic stainless steel alloy composition is observed. When compared to Figure 2 , which shows a micrograph of the austenitic stainless steel alloy composition of Example 2 , the grain size is decreased with the addition ofNb and V, regardless of whether the austenitic stainless steel alloy is press forged or hot rolled. Figure 3 shows a micrograph of the austenitic stainless steel alloy composition of Example 3, which includes Cu as well as the addition of Nb and V, and, also shows a decrease in grain size from the austenitic stainless steel alloy composition of Example 1.

[0031] As observed, the small addition of Nb and V significantly increased the annealed YS to a level higher than any currently available annealed austenitic stainless steel. Also, elements such as Ni, Cu, and Mo can be adjusted in the austenitic stainless steel alloy composition to obtain excellent corrosion resistance in chloride pitting and crevice conditions, as well as hydrogen sulfide environments.

[0032] Now, a method of manufacturing an austenitic stainless steel alloy composition according to the invention will be described. No special technique are required for melting and refining a nitrogen-containing alloy into an ingot or an electrode. Arc-melting followed by argon-oxygen decarburization (AOD)can be used.

[0033] If an electrode is cast after the AOD process then further refining will be performed using an electroslag remelting (ESR) process. The ESR process offers an austenitic stainless steel ingot to have improved qualities from the electrode by the formation of a solidified thin slag skin between ingot and mold wall during the remelting operation. During ESR process, the electrode is refined to reduce impurities, especially oxygen and sulfur. The ESR process also reduces segregation in the ingot. One skilled in the art should appreciate that other secondary melt processes may be using to perform the same function, including vacuum arc remelt (VAR). However, VAR may degrade the properties by loss ofN content in the electrode. Once the ESR process is complete, an ingot of steel alloy according to the invention is formed.

[0034] Next, the ingot may be hot worked. For instance, the ingot may be press or rotary forged at a temperature of 2000-2300 degrees F to large diameter bar and annealed. One skilled in the art should appreciate that these large diameter bars cannot be cold rolled due to their large section size and thus, final attained yield strength will be in the annealed condition, especially for optimum corrosion resistance. If hot rolling to smaller sizes then cold rolling can be performed.

[0035] While the invention has been described in detail and with reference to specific embodiments, one of ordinary skill in the art would appreciate that the described embodiments are illustrative, and that various changes and modifications can be made without departing from the scope of the invention.

Claims

1. An austenitic stainless steel alloy, comprising:

0.7-1.2 wt % of N;
10-25 wt % of Ni;
26-34 wt % of Cr;
0.1-1.0 wt % of Nb;
0.1-1.0 wt % of V; and

a balance of Fe and incidental impurities.

2. The austenitic stainless steel alloy according to claim 1, wherein there are one or more additional elements.

3. The austenitic stainless steel alloy according to claim 2, wherein the one or more additional elements are optionally C, Mo, Cu, Mn,. S, Si , or B.

4. The austenitic stainless steel alloy according to claim 3, wherein the one or more additional elements are optionally ≤ .08 wt % of C, ≤ 4.0 wt% of Mo, ≤ 4 wt% of Cu, 2.0 to 10.0 wt% of Mn, ≤ .01 wt% of S, ≤ 2 wt% of Si, ≤ .006 wt% of B

5. The austenitic stainless steel alloy according to claim 1, wherein the Nb is 0.1-.5 wt % .

6. The austenitic stainless steel alloy according to claim 5, wherein the Nb is 0.1-0.3 wt % .

7. The austenitic stainless steel alloy according to claim 5, wherein the V is 0.1-0.5 wt % .

8. The austenitic stainless steel alloy according to claim 7, wherein the V is 0.1-0.3 wt %.

9. The austenitic stainless steel alloy according to claim 7, wherein the Ni is 12-22 wt %.

10. The austenitic stainless steel alloy according to claim 9, wherein the Ni is 14-18 wt %.

11. The austenitic stainless steel alloy according to claim 9, wherein the Cr is 28-33 wt %.

12. The austenitic stainless steel alloy according to claim 11, wherein the Cr is 30-32 wt % Cr.

13. The austenitic stainless steel alloy according to claim 11, wherein the one or more additional elements are optionally C, Mo, Cu, Mn,. S, Si , or B.

14. The austenitic stainless steel alloy according to claim 13, wherein the one or more additional elements are optionally ≤ .05 wt % of C, wherein the C is preferably ≤ .03 wt, 0.5-3.0 wt% of Mo, wherein the Mo is preferably.075-1.50 wt %, ≤ 3 wt% of Cu, wherein the Cu is preferably 0.5-2.5 wt %, 3.0-8.0 wt% of Mn, wherein the Mn is preferably 4.0-7.0 wt %, ≤ .05 wt% of S, wherein the S is preferably ≤ .003 wt %, ≤ 1 wt% of Si,. wherein the S is preferably ≤ .003 wt %, .001-.005 wt% of B, wherein the B is is preferably .002-.004 wt %.

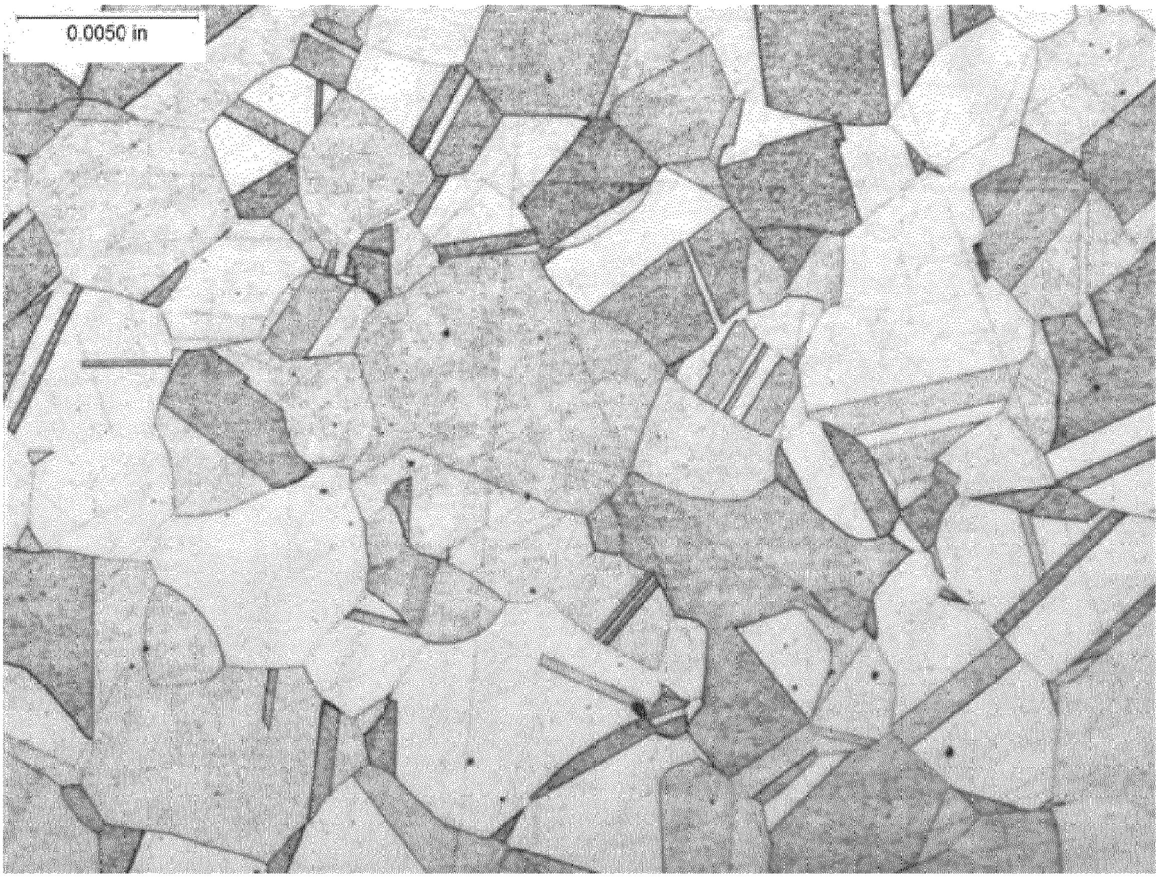

Figure 1

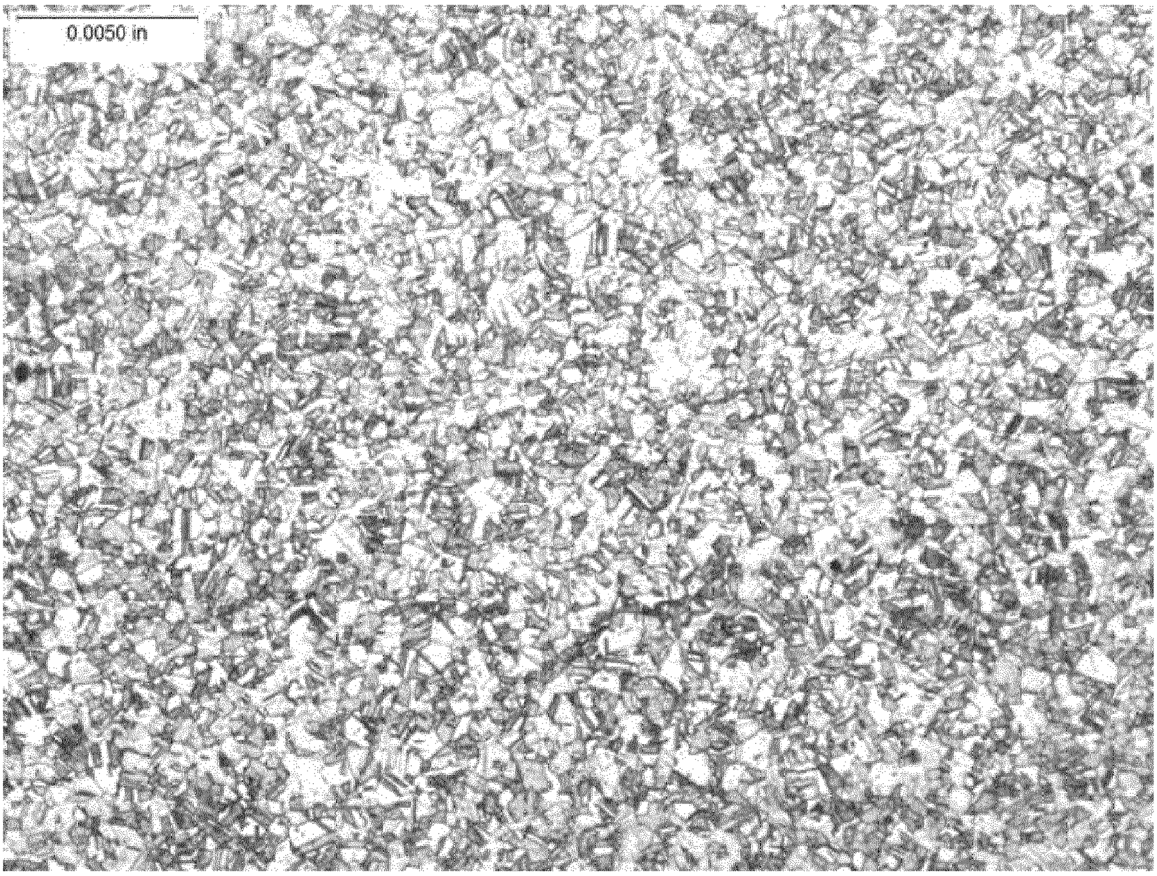

Figure 2

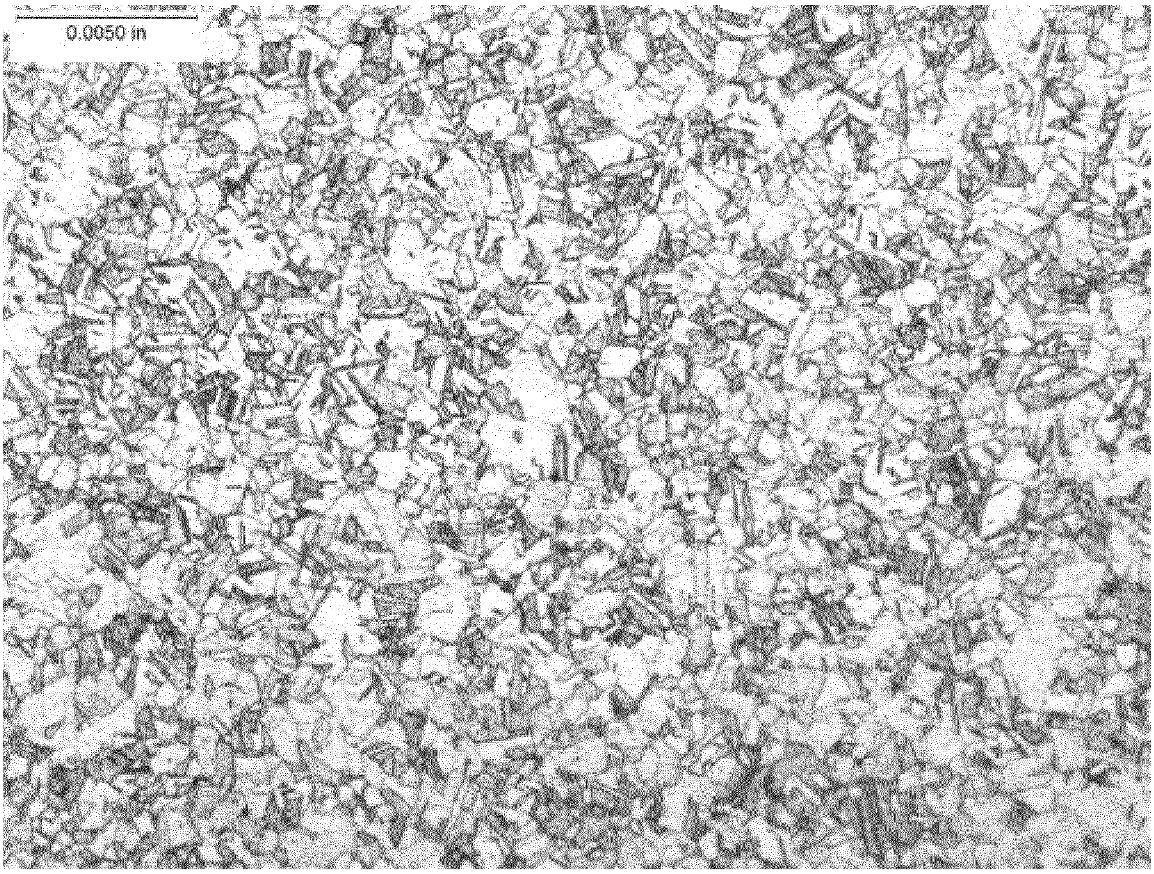

Figure 3

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EUROPEAN SEARCH REPORT

Application Number
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The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
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