



Office de la Propriété

Intellectuelle
du Canada

Un organisme
d'Industrie Canada

Canadian
Intellectual Property
Office

An agency of
Industry Canada

CA 2715998 C 2015/07/28

(11)(21) **2 715 998**

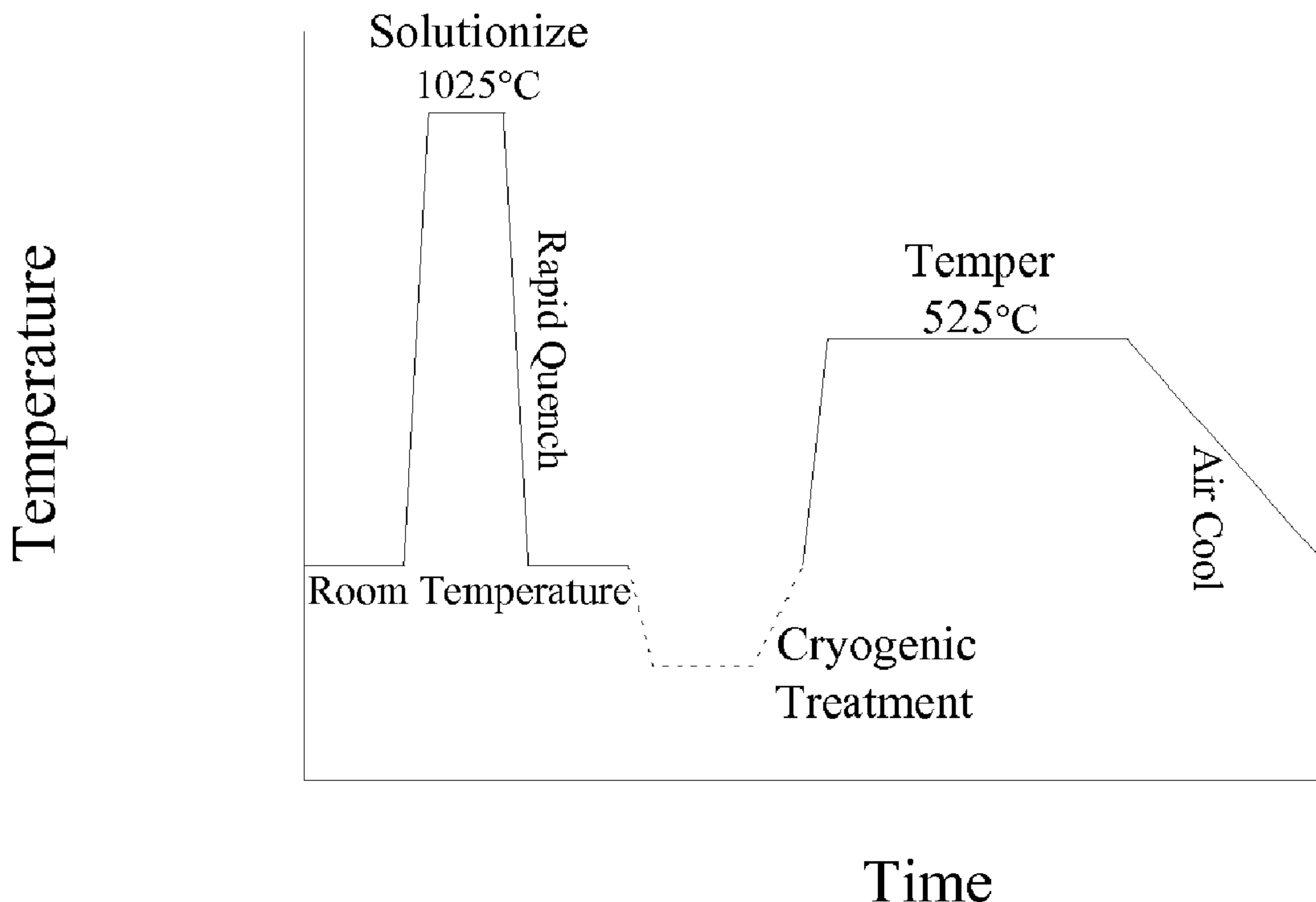
(12) **BREVET CANADIEN**
CANADIAN PATENT

(13) **C**

(86) Date de dépôt PCT/PCT Filing Date: 2009/02/20
(87) Date publication PCT/PCT Publication Date: 2009/10/29
(45) Date de délivrance/Issue Date: 2015/07/28
(85) Entrée phase nationale/National Entry: 2010/08/18
(86) N° demande PCT/PCT Application No.: US 2009/034720
(87) N° publication PCT/PCT Publication No.: 2009/131739
(30) Priorités/Priorities: 2008/02/20 (US61/029,970);
2008/09/18 (US61/098,037)

(51) Cl.Int./Int.Cl. *C21D 6/00*(2006.01),
C21D 6/02(2006.01), *C21D 6/04*(2006.01),
C22C 38/10(2006.01), *C22C 38/12*(2006.01)
(72) Inventeur/Inventor:
JOU, HERNG-JENG, US
(73) Propriétaire/Owner:
QUESTEK INNOVATIONS LLC, US
(74) Agent: SMART & BIGGAR

(54) Titre : ACIER A HAUTE TENACITE, A RESISTANCE EXTREMEMENT ELEVEE
(54) Title: ULTRA-HIGH-STRENGTH, HIGH-TOUGHNESS STEEL



(57) Abrégé/Abstract:

A non-stainless steel alloy includes, in combination by weight, about 0.20% to about 0.33% carbon, about 4.0% to about 8.0% cobalt, about 7.0 to about 11.0 % nickel, about 0.8% to about 3.0% chromium, about 0.5% to about 2.5% molybdenum, about 0.5% to about 5.9% tungsten, about 0.05% to about 0.20% vanadium, and up to about 0.02% titanium, the balance essentially iron and incidental elements and impurities.

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

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
29 October 2009 (29.10.2009)(10) International Publication Number
WO 2009/131739 A3(51) International Patent Classification:
C21D 6/00 (2006.01) **C22C 38/10** (2006.01)
C21D 6/02 (2006.01) **C22C 38/12** (2006.01)
C21D 6/04 (2006.01)
(21) International Application Number:
PCT/US2009/034720(22) International Filing Date:
20 February 2009 (20.02.2009)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
 61/029,970 20 February 2008 (20.02.2008) US
 61/098,037 18 September 2008 (18.09.2008) US
(71) Applicant (for all designated States except US):
QUESTEK INNOVATIONS LLC [US/US]; 1820 Ridge Avenue, Evanston, IL 60201 (US).

(72) Inventor; and

(75) Inventor/Applicant (for US only): **JOU, Herng-Jeng** [US/US]; 1210 Manor Drive, Wilmette, IL 60091 (US).(74) Agents: **SCHLENZ, Gregory, G.** et al.; Banner & Witcoff, Ltd., 10 S. Wacker Drive, Suite 3000, Chicago, IL 60606-7407 (US).

(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, ST, 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, MK, 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).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))

[Continued on next page]

(54) Title: LOWER-COST, ULTRA-HIGH-STRENGTH, HIGH-TOUGHNESS STEEL

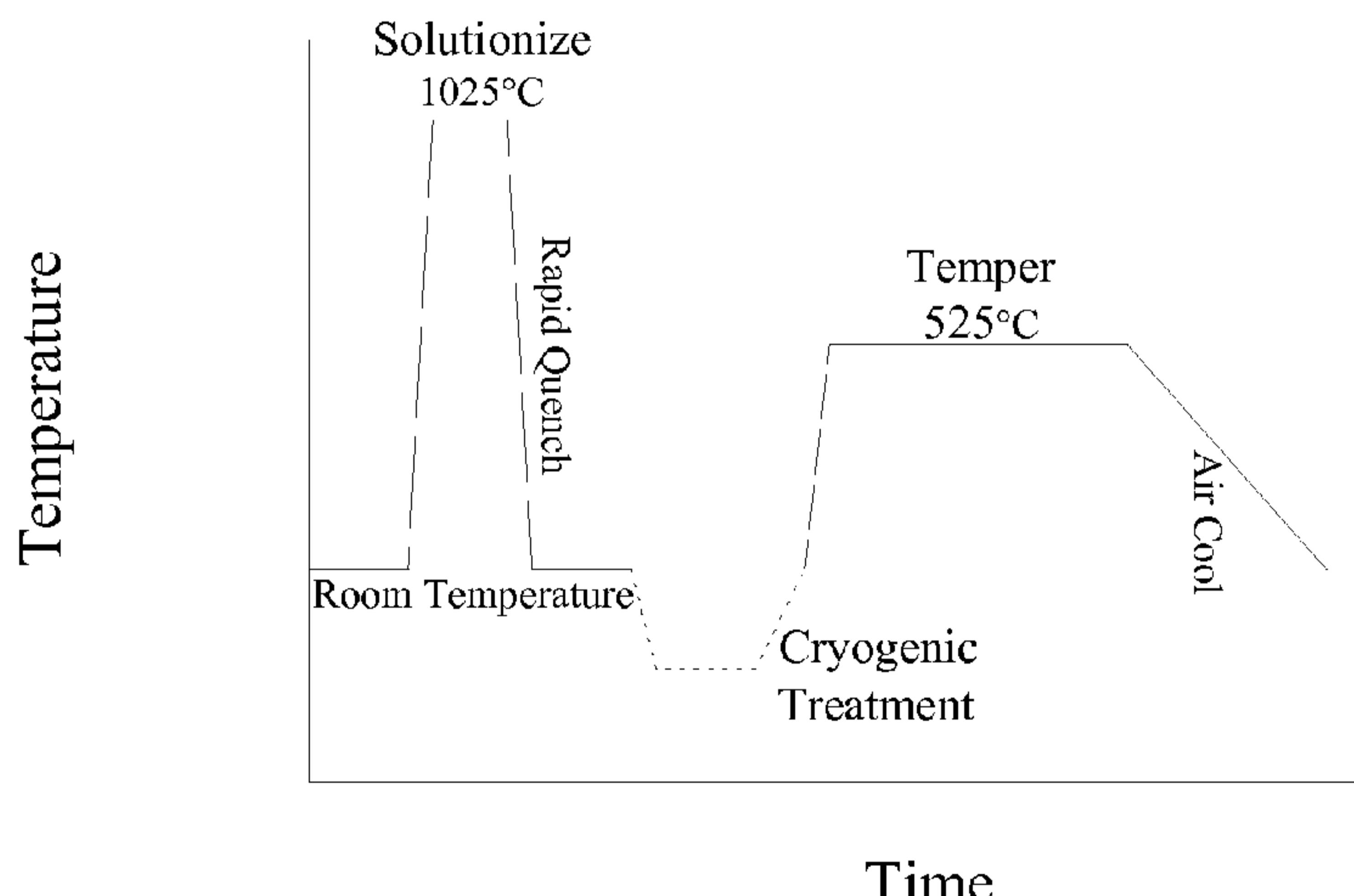


FIG. 2

(57) Abstract: A non-stainless steel alloy includes, in combination by weight, about 0.20% to about 0.33% carbon, about 4.0% to about 8.0% cobalt, about 7.0 to about 11.0 % nickel, about 0.8% to about 3.0% chromium, about 0.5% to about 2.5% molybdenum, about 0.5% to about 5.9% tungsten, about 0.05% to about 0.20% vanadium, and up to about 0.02% titanium, the balance essentially iron and incidental elements and impurities.

WO 2009/131739 A3

(88) Date of publication of the international search report:

11 February 2010

Published:

- *with international search report (Art. 21(3))*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

ULTRA-HIGH-STRENGTH, HIGH TOUGHNESS STEEL

[001]

[002]

TECHNICAL FIELD

[003] The invention relates to steel alloys, and more particularly, to steel alloys having ultra-high strength and high toughness with acceptable cost of production.

BACKGROUND

[004] AerMet[®] 100, disclosed in U.S. Patent Nos. 5,087,415 and 5,268,044, is a commercial ultra-high-strength, non-stainless steel which does not require case hardening. The nominal composition of AerMet 100 is 13.4 Co, 11.1 Ni, 3.1 Cr, 1.2 Mo, 0.23 C, and balance Fe, in wt%. AerMet 100 shows a suitable combination of high strength and fracture toughness for aircraft parts and ordnance. Additionally, AerMet 100 shows an ambient 0.2% yield stress of 1720 MPa and a Rockwell C-scale hardness of 53.0-54.0, with K_{IC} of 126 MPa \sqrt{m} . However, the alloying elements Co and Ni are rather costly, increasing the overall steel cost and constraining applications. Thus, there has developed a need for a steel with similar mechanical properties as AerMet 100 at a significantly lower cost.

[005] HY180, disclosed in U.S. Patent No. 3,502,462,

61368-1359(S)

is a commercial high-strength, non stainless steel which does not require case hardening. The nominal composition of HY180 is 10 Ni, 8 Co, 2 Cr, 1 Mo, 0.13 C, 0.1 Mn, 0.05 Si, and balance Fe, in wt%. While the material cost of HY180 is lower than AerMet 100, due to the lower Co addition, the ambient 0.2% yield stress of HY180 is limited to 1240 MPa.

[006] U.S. Patent No. 5,358,577, discloses a high strength, high toughness stainless steel with a nominal composition of 12-21 Co, 11-15 Cr, 0.5-3.0 Mo, 0-2.0 Ni, 0-2.0 Si, 0-1.0 Mn, 0.16-0.25 C, at least one element selected from the group consisting of 0.1-0.5 V and 0-0.1 Nb, and balance Fe, in wt%. This alloy shows an ambient Ultimate Tensile Strength (UTS) of 1720 MPa or greater and an ambient 0.2% yield stress of 1190 MPa or greater. However, the ambient 0.2% yield stress of this alloy is limited to about 1450 MPa, and furthermore, the material cost is high due to the high Co addition.

[007] Alloy disclosed in U.S. Patent Nos. 7,160,399 and 7,235,212, display ultra-high-strength, corrosion-resistant steels which do not require case hardening. The nominal composition of one alloy taught by the patents, branded as Ferrium S53®, is 14.0 Co, 10.0 Cr, 5.5 Ni, 2.0 Mo, 1.0 W, 0.30V, 0.21 C, and balance Fe, in wt%. Ferrium S53® exhibits an ambient UTS of about 1980 MPa and an ambient 0.2% yield stress of about 1560 MPa. The K_{IC} of Ferrium S53® is limited to about 72 MPa \sqrt{m} , and the material cost is high due to the high Co addition.

[008] U.S. Patent No. 6,176,946, discloses a class of steel alloys comprising a case hardened mixture with a core composition of 15-28 Co, 1.5-9.5 Ni, 0.05-0.25 C, and one or more additives selected from 3.5-9 Cr, less than 2.5 Mo, and less than 0.2 V and the balance Fe, in wt%. The mixture taught by the patent is case hardened in the range of surface hardness greater than a Rockwell C-scale hardness of 60. The class of steel alloys taught by the patent is thus distinct from AerMet 100, in that it requires case hardening and also targets a much higher surface hardness. In addition, the material cost for the class of steel alloys taught by the patent is high due to the high Co addition.

[009] The present alloy provides advantages such as ultra-high strength coupled with lower amounts of certain elements to thereby achieve lower cost. A full discussion of the features and advantages of the present invention is deferred to the following detailed

description, which proceeds with reference to the accompanying drawings.

BRIEF SUMMARY

- [010] Aspects of the invention relate to a steel alloy that includes, in combination by weight: about 0.20% to about 0.33% carbon, about 4.0% to about 8.0% cobalt, about 7.0 to about 11.0 % nickel, about 0.8% to about 3.0% chromium, about 0.5% to about 2.5% molybdenum, about 0.5% to about 5.9% tungsten, about 0.05% to about 0.20% vanadium, and up to about 0.02% titanium, the balance essentially iron and incidental elements and impurities.
- [011] According to one aspect, the alloy includes, in combination by weight, about 0.25% to about 0.31% carbon, about 6.8% to about 8.0% cobalt, about 9.3 to about 10.5% nickel, about 0.8% to about 2.6% chromium, about 0.9% to about 2.1% molybdenum, about 0.7% to about 2.0% tungsten, about 0.05% to about 0.12% vanadium, and up to about 0.015% titanium, the balance essentially iron and incidental elements and impurities. In another aspect, the alloy includes, in combination by weight, about 0.29% to about 0.31% carbon, about 6.8% to about 7.2% cobalt, about 9.8 to about 10.2 % nickel, about 0.8% to about 2.6% chromium, about 0.9% to about 2.1% molybdenum, about 0.7% to about 1.4% tungsten, about 0.05% to about 0.12% vanadium, and up to about 0.015% titanium, the balance essentially iron and incidental elements and impurities.
- [012] According to another aspect, the alloy is strengthened at least in part by M_2C carbide precipitates, where M includes one or more elements selected from the group consisting of: Cr, Mo, W, and V.
- [013] According to a further aspect, the alloy has a predominately lath martensite microstructure.
- [014] According to a still further aspect, the alloy has an ultimate tensile strength of at least about 1900 MPa, and a K_{IC} fracture toughness of at least about 110 MPa \sqrt{m} .
- [015] Additional aspects of the invention relate to a method for processing a steel alloy that includes, in combination by weight, about 0.20% to about 0.33% carbon, about 4.0% to about 8.0% cobalt, about 7.0 to about 11.0 % nickel, about 0.8% to about 3.0% chromium, about 0.5% to about 2.5% molybdenum, about 0.5% to about 5.9% tungsten, about 0.05% to about 0.20% vanadium, and up to about 0.02% titanium, the balance essentially iron and incidental elements and impurities. The method includes subjecting the alloy to a solutionizing heat treatment at 950°C to 1100°C for 60-90 minutes and

61368-1359

then to a tempering heat treatment at 465°C to 550°C for 4-32 hours.

- [016] According to one aspect, the alloy includes, in combination by weight, about 0.25% to about 0.31% carbon, about 6.8% to about 8.0% cobalt, about 9.3 to about 10.5% nickel, about 0.8% to about 2.6% chromium, about 0.9% to about 2.1% molybdenum, about 0.7% to about 2.0% tungsten, about 0.05% to about 0.12% vanadium, and up to about 0.015% titanium, the balance essentially iron and incidental elements and impurities. In another aspect, the alloy includes, in combination by weight, about 0.29% to about 0.31% carbon, about 6.8% to about 7.2% cobalt, about 9.8 to about 10.2 % nickel, about 0.8% to about 2.6% chromium, about 0.9% to about 2.1% molybdenum, about 0.7% to about 1.4% tungsten, about 0.05% to about 0.12% vanadium, and up to about 0.015% titanium, the balance essentially iron and incidental elements and impurities.
- [017] According to another aspect, the method includes quenching the alloy after the solutionizing heat treatment, and air cooling the alloy after the tempering heat treatment.
- [018] According to a further aspect, the method further includes subjecting the alloy to a cryogenic treatment between the solutionizing heat treatment and the tempering heat treatment.
- [019] According to a still further aspect, the alloy has a resultant predominately lath martensite microstructure and includes M₂C carbide precipitates, where M includes one or more elements selected from the group consisting of: Cr, Mo, W, and V.

61368-1359

4a

[019a] A still further aspect of the invention relates to a non-stainless steel alloy comprising, in combination by weight: about 0.20% to about 0.33% carbon, about 4.0% to about 8.0% cobalt, about 7.0 to about 11.0% nickel, about 1.0% to about 3.0% chromium, about 0.5% to about 2.5% molybdenum, about 0.5% to about 5.9% tungsten, about 0.05% to about 0.20% 5 vanadium, and up to about 0.02% titanium, the balance essentially iron and incidental elements and impurities, wherein the alloy has a predominately lath martensite microstructure and is strengthened at least in part by M_2C carbide precipitates which measure less than about 20 nm in the longest dimension, where M comprises one or more elements selected from the group consisting of: Mo, Cr, W, and V, and wherein the alloy has an ultimate tensile 10 strength of at least about 1900 MPa and a K_{IC} fracture toughness of at least about 110 MPa \sqrt{m} .

[019b] A still further aspect of the invention relates to a non-stainless steel alloy comprising, in combination by weight: 0.20% to 0.33% carbon, 4.0% to 8.0% cobalt, 7.0 to 11.0% nickel, 0.8% to 3.0% chromium, 0.5% to 2.5% molybdenum, 0.5% to 5.9% tungsten, 0.05% to 0.20% 15 vanadium, and up to 0.02% titanium, the balance iron and impurities.

[019c] A still further aspect of the invention relates to a method comprising: providing a steel alloy comprising, in combination by weight, 0.20% to 0.33% carbon, 4.0% to 8.0% cobalt, 7.0 to 11.0% nickel, 0.8% to 3.0% chromium, 0.5% to 2.5% molybdenum, 0.5% to 5.9% tungsten, 0.05% to 0.20% vanadium, and up to 0.02% titanium, the balance iron and 20 impurities; subjecting the alloy to a solutionizing heat treatment at 950°C to 1100°C for 60-90 minutes, and optionally quenching the alloy after the solutionizing heat treatment; optionally, subjecting the alloy to a cryogenic treatment after the solutionizing heat treatment; and subjecting the alloy to a tempering heat treatment at 465°C to 550°C for 4-32 hours, and optionally air cooling the alloy after the tempering heat treatment.

[019d] A still further aspect of the invention relates to a non-stainless steel alloy comprising, in combination by weight: 0.20% to 0.33% carbon, 4.0% to 8.0% cobalt, 7.0 to 11.0% nickel, 0.8% to 3.0% chromium, 0.5% to 2.5% molybdenum, 0.5% to 5.9% tungsten, 0.05% to 0.20% vanadium, and titanium, wherein the amount of titanium is more than 0, less than or equal 25

61368-1359

4b

to 0.02wt% of the alloy, the balance essentially iron and incidental elements and impurities; wherein the non-stainless steel alloy further includes Ti-enriched carbides, and the alloy is strengthened at least in part by M_2C carbide precipitates which measure less than 20 nm in the longest dimension.

5 [019e] A still further aspect of the invention relates to a method comprising: providing a steel alloy comprising, in combination by weight, 0.20% to 0.33% carbon, 4.0% to 8.0% cobalt, 7.0 to 11.0% nickel, 0.8% to 3.0% chromium, 0.5% to 2.5% molybdenum, 0.5% to 5.9% tungsten, 0.05% to 0.20% vanadium, and up to 0.02% titanium, the balance essentially iron and incidental elements and impurities; subjecting the alloy to a solutionizing heat treatment 10 at 950°C to 1100°C for 60-90 minutes; and subjecting the alloy to a tempering heat treatment at 465°C to 550°C for 4-32 hours; wherein the non-stainless steel alloy further includes Ti-enriched carbides, and the alloy is strengthened at least in part by M_2C carbide precipitates which measure less than 20 nm in the longest dimension.

[019f] A still further aspect of the invention relates to a non-stainless steel alloy comprising, 15 in combination by weight: 0.20% to 0.33% carbon, 4.0% to 8.0% cobalt, 7.0 to 11.0% nickel, 1.0% to 3.0% chromium, 0.5% to 2.5% molybdenum, 0.5% to 5.9% tungsten, 0.05% to 0.20% vanadium, and titanium, wherein the amount of titanium is more than 0, less than or equal to 0.02wt% of the alloy, the balance essentially iron and incidental elements and impurities, wherein the alloy has a predominately lath martensite microstructure and is strengthened at 20 least in part by M_2C carbide precipitates which measure less than 20 nm in the longest dimension, where M comprises one or more elements selected from the group consisting of: Mo, Cr, W, and V, and wherein the alloy has an ultimate tensile strength of at least 1900 MPa and a K_{IC} fracture toughness of at least 110 MPam^{1/2}; wherein the non-stainless steel alloy further includes Ti-enriched carbides.

25 [019g] A still further aspect of the invention relates to a non-stainless steel alloy consisting of, in combination by weight: 0.20% to 0.33% carbon, 4.0% to 8.0% cobalt, 7.0 to 11.0% nickel, 0.8% to 3.0% chromium, 0.5% to 2.5% molybdenum, 0.5% to 5.9% tungsten, 0.05% to 0.20% vanadium, and up to 0.02% titanium, the balance iron and impurities.

61368-1359

4c

[019h] A still further aspect of the invention relates to a method comprising: providing a steel alloy consisting of, in combination by weight, 0.20% to 0.33% carbon, 4.0% to 8.0% cobalt, 7.0 to 11.0% nickel, 0.8% to 3.0% chromium, 0.5% to 2.5% molybdenum, 0.5% to 5.9% tungsten, 0.05% to 0.20% vanadium, and up to 0.02% titanium, the balance iron and
5 impurities; subjecting the alloy to a solutionizing heat treatment at 950°C to 1100°C for 60-90 minutes; and subjecting the alloy to a tempering heat treatment at 465°C to 550°C for 4-32 hours, wherein the alloy may be subjected to a cryogenic treatment between the solutionizing heat treatment and the tempering heat treatment.

[019i] A still further aspect of the invention relates to a non-stainless steel alloy comprising,
10 in combination by weight: about 0.20% to about 0.33% carbon, about 4.0% to about 8.0% cobalt, about 7.0 to about 11.0% nickel, about 0.8% to about 3.0% chromium, about 0.5% to about 2.5% molybdenum, about 0.5% to about 5.9% tungsten, about 0.05% to about 0.20% vanadium, and titanium up to about 0.02%, the balance essentially iron and incidental elements and impurities having a microstructure characterized by M_1C grain refinement
15 particles wherein M_1 is comprised of Ti and by inclusion of principally M_2C carbide particle precipitates wherein M_2 is comprised of chromium (Cr), molybdenum (Mo), tungsten (W), and vanadium (V) and in a predominately lath martensite cobalt-nickel (Co, Ni) matrix, said alloy further characterized by the combination of high strength and high fracture toughness.

[020] Other features and advantages of the invention will be apparent from the following
20 specification taken in conjunction with the following drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[021] In the detailed description which follows, reference will be made to the drawings comprised of the following figures:

[022] FIG. 1 shows a plurality of composition windows, defined by the calculated Vickers
25 hardness number and solution temperature;

61368-1359

4d

[023] FIG. 2 is a schematic illustration of one embodiment of processing an alloy according to the invention, indicating the time and temperature of processing steps of the method embodiment;

[024] FIG. 3 is a graph illustrating the ultimate tensile strength and K_{IC} fracture toughness of 5 AerMet 100 and two embodiments of alloys (A and B) according to the invention;

[025] FIG. 4 is a graph illustrating the Rockwell C-scale hardness and K_{IC} fracture toughness of AerMet 100 and one embodiment of an alloy (A) according to the invention, at specified tempering conditions; and

[026] FIG. 5 is a potentiogram comparing the stress-corrosion cracking resistance (K_{ISCC}) of one embodiment of an alloy (A) according to the invention and AerMet 100, in solid and open circles, respectively.

DETAILED DESCRIPTION

[027] While this invention is susceptible of embodiments in many different forms, exemplary embodiments of the invention are referenced in the drawings and will herein be described in detail with the understanding that the present disclosure is to be considered as an exemplification of the principles of the invention and is not intended to limit the broad aspect of the invention to the embodiments illustrated.

[028] According to embodiments of the present invention, a steel alloy is provided that includes an alloying addition of Co that is lower than that of AerMet 100 and other alloying additions that include W and V. The lower Co content of the invented steel can reduce the thermodynamic driving force of M_2C formation. However, the M_2C formation during tempering assists in obtaining increased strength. The addition of elements such as W and V can assist in achieving a sufficient driving force of M_2C formation to obtain the desired strength. Embodiments of the alloy can be processed so that the alloy comprises a predominantly lath martensitic matrix and is strengthened by a fine-scale distribution of M_2C carbides. In one embodiment, the M_2C carbides measure less than about 20 nm in the longest dimension and comprise the alloying elements of Mo, Cr, W, and V.

[029] FIG. 1 illustrates a composition window of Mo and W according to one embodiment of the alloy, defined by the calculated Vickers hardness number and solution temperature. In the embodiment described in FIG. 1, the amount of Mo is kept below about 2.5 wt% to avoid microsegregation during solidification of the ingot, and the solution temperature is kept below about 1100°C to avoid undesirable grain growth. In this embodiment, the addition of W allows for a higher tempering temperature, which can enable the co-precipitation of M_2C and austenite, promoting transformation-induced plasticity and improving toughness. The addition of W can also enable a robust design which tolerates slight variations in tempering and provide the unexpected benefit of

enhancing resistance to stress corrosion cracking. In this embodiment, the steel further includes Ti-enriched carbides that can operate to refine the grain size and enhance toughness and strength.

- [030] In one example embodiment, an alloy is provided that includes (in wt.%) about 0.20% to about 0.33% carbon (C), about 4.0% to about 8.0% cobalt (Co), about 7.0 to about 11.0 % nickel (Ni), about 0.8% to about 3.0% chromium (Cr), about 0.5% to about 2.5% molybdenum (Mo), about 0.5% to about 5.9% tungsten (W), about 0.05% to about 0.20% vanadium (V), and up to about 0.02% titanium (Ti), the balance being essentially iron (Fe) and incidental elements and impurities.
- [031] In another embodiment, the alloy includes, in combination by weight, about 0.25% to about 0.31% carbon, about 6.8% to about 8.0% cobalt, about 9.3 to about 10.5 % nickel, about 0.8% to about 2.6% chromium, about 0.9% to about 2.1% molybdenum, about 0.7% to about 2.0% tungsten, about 0.05% to about 0.12% vanadium, and up to about 0.015% titanium, the balance essentially iron and incidental elements and impurities.
- [032] In yet another embodiment, the alloy comprises, in combination by weight, about 0.29% to about 0.31% carbon, about 6.8% to about 7.2% cobalt, about 9.8 to about 10.2 % nickel, about 0.8% to about 2.6% chromium, about 0.9% to about 2.1% molybdenum, about 0.7% to about 1.4% tungsten, about 0.05% to about 0.12% vanadium, and up to about 0.015% titanium, the balance essentially iron and incidental elements and impurities.
- [033] As stated above, the alloy is strengthened at least in part by M₂C metal carbides. In various embodiments, the alloy may contain metal carbides where M is one or more elements selected from the group consisting of Mo, Cr, W, and V, and may have amounts of each element (if present) decreasing in the order listed, i.e., Mo in the largest concentration, followed by Cr, W, and/or V. In other embodiments, the alloy may contain different amounts of these elements.
- [034] Alloys as described herein can be processed in a variety of different manners. In one embodiment, illustrated in FIG. 2, the alloy is first subjected to a solutionizing heat treatment, then rapidly quenched, followed by a tempering heat treatment and air cooling. In one embodiment, the solutionizing heat treatment can be carried out at temperatures in the range of 950°C to 1100°C for 60-90 minutes, and the tempering heat treatment can be carried out at temperatures in the range of 465°C to 550°C for 4-32 hours. The Examples below illustrate further embodiments of methods for

processing the alloy, including different solutionizing treatments and tempering treatments. A cryogenic treatment may also optionally be employed between the solutionizing heat treatment and the tempering heat treatment, such as by immersing in liquid nitrogen for 1-2 hours and then warming to room temperature.

EXAMPLES

[035] Several example embodiments of alloys according to the invention are described below. Table I lists the measured compositions of each alloy embodiment discussed in the Examples below, along with the nominal composition of commercial steel AerMet 100.

Table I

Alloys	Composition in wt%, Fe Balanced							
	C	Co	Ni	Cr	Mo	W	V	Ti
A	0.29	7.17	10.46	1.02	2.00	1.28	0.10	<0.01
B	0.27	6.96	9.79	0.95	1.40	1.16	0.08	0.01
C	0.28	6.74	9.60	0.76	1.34	1.04	0.07	0.01
D	0.28	6.94	10.2	2.62	0.94	0.72	0.046	0.01
AerMet 100	0.23	13.4	11.1	3.1	1.2	—	—	—

[036] Each of the alloy embodiments in Table I was subjected to processing steps such as those described in FIG. 2, including solutionizing heat treatment and/or tempering heat treatment, as detailed in the Examples described below. Additionally, various tests were performed on the alloys, such as testing one or more physical properties of the alloys, as also detailed in the Examples below.

EXAMPLE A

[037] A 300-lb vacuum induction melt of alloy A was prepared from high purity materials. The melt was converted to a 3-inch-round-corner-square bar. The alloy was subjected to a solutionizing heat treatment at 1025°C for 90 minutes, quenched with oil, immersed in liquid nitrogen for 2 hours, warmed in air to room temperature, and then the samples were each subjected to one of several different tempering heat treatments identified in Table II below and cooled in air. The amounts of Ni and C of alloy A served to place the martensite start temperature (M_s) above about 200°C, and M_s was confirmed for this alloy as 222°C, using dilatometry. Transmission electron microscopy and atom probe

tomography verified the presence of M_2C , along with grain refining carbides in specimens tempered at 525°C for 12 hours or 550°C for 4 hours. The Charpy V-Notch (CVN) impact energy at -40°C and tensile strength at room temperature were measured for various tempering conditions, using two samples per each condition. These results are also shown in Table II.

Table II

Tempering		Ambient 0.1% Yield Stress (MPa)	Charpy V-Notch Energy (ft·lb) at -40°C
525°C	4h	1669± 6	28.5±1.5
	6h	1683± 9	28.5±2.5
	8h	1697± 3	33.5±3.5
	12h	1685± 8	32.0±0.0
535°C	4h	1660± 4	28.0±1.0
	6h	1626±19	21.5±1.5
	8h	1666±10	29.5±0.5
550°C	4h	1667± 6	23.0±1.0

[038] The ultimate tensile strength (UTS), K_{IC} fracture toughness, and Rockwell-C hardness were also measured for samples of alloy A. FIG. 3 illustrates a comparison of the UTS and the K_{IC} fracture toughness for the measured samples, and FIG. 4 illustrates a comparison of the Rockwell-C hardness and the K_{IC} fracture toughness for the measured samples. As shown in FIG. 3, alloy A was found to have a comparable and/or superior combination of strength and toughness compared to AerMet 100 in its preferred tempering at 482°C, in particular the samples of alloy A that were tempered at 525°C. Furthermore, alloy A was found to demonstrate a robust design with a built-in tolerance for slight variations in tempering time. The optimum tempering heat treatment in this experiment was found to be 525°C for 6 hours, although other heat treatments were found to produce positive results. A comparison of the measured properties of alloy A tempered at 525°C for 6 hours and the properties of AerMet 100 are shown in Table III below.

Table III

	Ambient 0.2% Yield Stress (MPa)	Ambient Ultimate Tensile Stress (MPa)	Elongation (%)	Reduction of Area (%)	Ambient Charpy V-Notch Energy (ft·lb)	Ambient K_{IC} (MPa \sqrt{m})
Alloy A	1800	1990	14	66	37	122
AerMet 100	1720	1960	14	65	30	126

[039] Additionally, samples of alloy A were tested for stress corrosion cracking resistance (K_{ISCC}) at various applied electrical potentials, using the ASTM F1624/F1940 Standard Test Method for Measurement of Hydrogen Embrittlement in Steel by Incremental Loading Technique. Twelve specimens of alloy A were compared to twelve specimens of AerMet 100, and the results of such testing are shown in FIG. 5. The measured K_{ISCC} , or the fracture toughness in stress corrosion cracking, of alloy A was found to be far superior to that of AerMet 100, at Open-Circuit Potential (OCP) (about -0.6V for these steels). As shown in FIG. 5, whereas AerMet 100 maintained only about 20% of its fracture toughness in moving from ambient to OCP, alloy A maintained about 90% of its fracture toughness at OCP. For comparison, Ferrium S53[®] has been found to maintain about 77% of its fracture toughness at OCP. The improvement in stress cracking corrosion resistance of Alloy A was unexpected.

EXAMPLE B

[040] A 300-lb vacuum induction melt of alloy B was prepared from high purity materials. The melt was converted to a 3-inch-round-corner-square bar. The alloy was subjected to a solutionizing heat treatment at 1025°C for 90 minutes, quenched with oil, immersed in liquid nitrogen for 2 hours, and warmed in air to room temperature, and then the samples were each subjected to one of several different tempering heat treatments identified in Table IV below and cooled in air. The amounts of Ni and C of alloy B served to place M_s above about 200°C, and M_s was confirmed for this alloy as 286°C using dilatometry. The CVN impact energy at -40°C and tensile strength at room temperature were measured for various tempering conditions, using two samples per each condition. These results are also listed in Table IV.

Table IV

Tempering		Ambient 0.1% Yield Stress (MPa)	Charpy V-Notch Energy (ft·lb) at -40°C
510°C	12h	1566± 4	34.5±2.1
	16h	1579± 3	33.0±2.8
525°C	8h	1553±17	36.5±0.7

[041] The ultimate tensile strength (UTS) and K_{IC} fracture toughness were also measured for samples of alloy B, as indicated in FIG. 3. Alloy B was found to have mechanical characteristics equal to or better than those of AerMet 100, and the optimum tempering

heat treatment in this experiment was found to be 525°C for 8 hours, although other heat treatments were found to produce positive results.

EXAMPLE C

[042] A 300-lb vacuum induction melt of alloy C was prepared from high purity materials. The melt was converted to a 3-inch-round-corner-square bar. The alloy was subjected to a solutionizing heat treatment at 1025°C for 90 minutes, quenched with oil, immersed in liquid nitrogen for 2 hours, and warmed in air to room temperature, and then the samples were each subjected to one of several different tempering heat treatments identified in Table V below, and cooled in air. The amounts of Ni and C of alloy C served to place M_s above about 200°C, and M_s was confirmed for this alloy as 247°C using dilatometry. The CVN impact energy at -40°C and tensile strength at room temperature were measured for various tempering conditions, using two samples per each condition. These results are also listed in Table V.

Table V

Tempering		Ambient 0.1% Yield Stress (MPa)	Charpy V-Notch Energy (ft·lb) at -40°C
510°C	12h	1546±11	27.5±0.7
	16h	1561± 6	30.0±0.0
525°C	8h	1552± 7	29.5±2.1

[043] Alloy C was found to have mechanical characteristics comparable to those of AerMet 100, and the optimum tempering heat treatment in this experiment was found to be 510°C for 16 hours, although other heat treatments were found to produce positive results.

EXAMPLE D

[044] A 300-lb vacuum induction melt of alloy A was prepared from high purity materials. The melt was converted to a 3-inch-round-corner-square bar. The alloy was subjected to a solutionizing heat treatment at 950°C for 60 minutes, quenched with oil, immersed in liquid nitrogen for 1 hour, and warmed in air to room temperature, and then subjected to a tempering heat treatment at 468°C for 32 hours or at 482°C for 16 hours and cooled in air. The CVN impact energy at -40°C, fracture toughness K_{IC} at room temperature, and tensile strength at room temperature were measured for various tempering conditions. The results of this testing are listed in Table VI below.

Table VI

Tempering	Ambient 0.2% Yield Stress (MPa)	Charpy V-Notch Energy (ft·lb) at -40°C	Ambient K _{Ic} (MPa√m)
468°C	32h	1650± 0	33.5±2.1
482°C	16h	1628± 5	36.0±0.0

[045] Alloy D was found to have mechanical characteristics comparable to those of AerMet 100, and neither of the tempering heat treatments in this experiment were found to be comparatively optimum, as both heat treatments were found to produce positive results.

[046] The various embodiments of alloys described herein, processed in the manners described herein, were found to have a comparable or even superior physical properties compared to existing alloys, such as AerMet 100. In particular, the alloy was found to be capable of providing a desirable combination of high tensile strength and high fracture toughness, a robust design which tolerates slight variations in tempering conditions, and the unexpected benefit of enhanced stress corrosion cracking resistance. Additionally, the comparatively smaller alloying additions of Co and Ni reduce the cost of the alloy as compared to existing alloys, such as AerMet 100. It is understood that further benefits and advantages are readily recognizable to those skilled in the art.

[047] Several alternative embodiments and examples have been described and illustrated herein. A person of ordinary skill in the art would appreciate the features of the individual embodiments, and the possible combinations and variations of the components. A person of ordinary skill in the art would further appreciate that any of the embodiments could be provided in any combination with the other embodiments disclosed herein. It is understood that the invention may be embodied in other specific forms without departing from the spirit or central characteristics thereof. The present examples and embodiments, therefore, are to be considered in all respects as illustrative and not restrictive, and the invention is not to be limited to the details given herein. Accordingly, while the specific embodiments have been illustrated and described, numerous modifications come to mind without significantly departing from the spirit of the invention and the scope of protection is only limited by the scope of the accompanying claims.

61368-1359(S)

12

CLAIMS:

1. A non-stainless steel alloy comprising, in combination by weight:
about 0.20% to about 0.33% carbon, about 4.0% to about 8.0% cobalt, about 7.0 to about 11.0% nickel, about 0.8% to about 3.0% chromium, about 0.5% to about 2.5%
5 molybdenum, about 0.5% to about 5.9% tungsten, and about 0.05% to about 0.20% vanadium, the balance essentially iron and incidental elements and impurities.
2. The alloy of claim 1, further comprising up to about 0.02% titanium.
3. The alloy of claim 2, wherein the alloy comprises, in combination by weight:
about 0.25% to about 0.31% carbon, about 6.8% to about 8.0% cobalt, about 9.3 to about
10 10.5% nickel, about 0.8% to about 2.6% chromium, about 0.9% to about 2.1% molybdenum, about 0.7% to about 2.0% tungsten, about 0.05% to about 0.12% vanadium, and up to about 0.015% titanium, the balance essentially iron and incidental elements and impurities.
4. The alloy of claim 2, wherein the alloy comprises, in combination by weight:
about 0.29% to about 0.31% carbon, about 6.8% to about 7.2% cobalt, about 9.8 to about
15 10.2% nickel, about 0.8% to about 2.6% chromium, about 0.9% to about 2.1% molybdenum, about 0.7% to about 1.4% tungsten, about 0.05% to about 0.12% vanadium, and up to about 0.015% titanium, the balance essentially iron and incidental elements and impurities.
5. The alloy of claim 1 or 2, wherein the alloy is strengthened at least in part by M₂C carbide precipitates which measure less than about 20 nm in the longest dimension.
- 20 6. The alloy of claim 5, wherein the alloy comprises M₂C precipitates where M comprises one or more elements selected from the group consisting of: Mo, Cr, W, and V.
7. The alloy of claim 1 or 2, wherein the alloy has a predominately lath martensite microstructure.
8. The alloy of claim 1 or 2, wherein the alloy has an ultimate tensile strength of
25 at least about 1900 MPa.

61368-1359(S)

13

9. The alloy of claim 1 or 2, wherein the alloy has a K_{IC} fracture toughness of at least about 110 MPa \sqrt{m} .

10. A method for processing a steel alloy, the method comprising:

providing a steel alloy comprising, in combination by weight, about 0.20% to 5 about 0.33% carbon, about 4.0% to about 8.0% cobalt, about 7.0 to about 11.0% nickel, about 0.8% to about 3.0% chromium, about 0.5% to about 2.5% molybdenum, about 0.5% to about 5.9% tungsten, and about 0.05% to about 0.20% vanadium, the balance essentially iron and incidental elements and impurities;

subjecting the alloy to a solutionizing heat treatment at 950°C to 1100°C for 10 60-90 minutes; and

subjecting the alloy to a tempering heat treatment at 465°C to 550°C for 4-32 hours.

11. The method of claim 10, wherein the steel alloy further comprises up to about 0.02% titanium.

15 12. The method of claim 11, wherein the alloy comprises, in combination by weight, about 0.25% to about 0.31% carbon, about 6.8% to about 8.0% cobalt, about 9.3 to about 10.5% nickel, about 0.8% to about 2.6% chromium, about 0.9% to about 2.1% molybdenum, about 0.7% to about 2.0% tungsten, about 0.05% to about 0.12% vanadium, and up to about 0.015% titanium, the balance essentially iron and incidental elements and 20 impurities.

13. The method of claim 11, wherein the alloy comprises, in combination by weight, about 0.29% to about 0.31% carbon, about 6.8% to about 7.2% cobalt, about 9.8 to about 10.2% nickel, about 0.8% to about 2.6% chromium, about 0.9% to about 2.1% molybdenum, about 0.7% to about 1.4% tungsten, about 0.05% to about 0.12% vanadium, and 25 up to about 0.015% titanium, the balance essentially iron and incidental elements and impurities.

61368-1359(S)

14

14. The method of claim 10 or 11, further comprising:

quenching the alloy after the solutionizing heat treatment; and

air cooling the alloy after the tempering heat treatment.

15. The method of claim 10 or 11, further comprising:

5 subjecting the alloy to a cryogenic treatment between the solutionizing heat treatment and the tempering heat treatment.

16. The method of claim 10 or 11, wherein the alloy has a resultant predominately lath martensite microstructure.

17. The method of claim 10 or 11, wherein the alloy has a resultant microstructure 10 comprising M_2C carbide precipitates which measure less than about 20 nm in the longest dimension.

18. The method of claim 17, wherein the M of the M_2C carbide precipitates comprises one or more elements selected from the group consisting of: Mo, Cr, W, and V.

19. The alloy of claim 1 or 2,

15 wherein the alloy has a predominately lath martensite microstructure and is strengthened at least in part by M_2C carbide precipitates which measure less than about 20 nm in the longest dimension, where M comprises one or more elements selected from the group consisting of: Mo, Cr, W, and V, and

wherein the alloy has an ultimate tensile strength of at least about 1900 MPa 20 and a K_{IC} fracture toughness of at least about 110 MPa \sqrt{m} .

20. The alloy of claim 19, wherein the alloy comprises, in combination by weight: about 0.25% to about 0.31% carbon, about 6.8% to about 8.0% cobalt, about 9.3 to about 10.5% nickel, about 0.8% to about 2.6% chromium, about 0.9% to about 2.1% molybdenum,

61368-1359(S)

15

about 0.7% to about 2.0% tungsten, about 0.05% to about 0.12% vanadium, and up to about 0.015% titanium, the balance essentially iron and incidental elements and impurities.

21. The alloy of claim 19, wherein the alloy comprises, in combination by weight:

about 0.29% to about 0.31% carbon, about 6.8% to about 7.2% cobalt, about 9.8 to about

5 10.2% nickel, about 0.8% to about 2.6% chromium, about 0.9% to about 2.1% molybdenum, about 0.7% to about 1.4% tungsten, about 0.05% to about 0.12% vanadium, and up to about 0.015% titanium, the balance essentially iron and incidental elements and impurities.

22. The method of claim 10 or 11, further comprising

optionally, subjecting the alloy to a cryogenic treatment after the solutionizing

10 heat treatment; and

subjecting the alloy to a tempering heat treatment at 465°C to 550°C for 4-32 hours, and optionally air cooling the alloy after the tempering heat treatment.

23. The method of claim 22, wherein the alloy has a resultant predominately lath martensite microstructure.

15 24. The method of claim 22 or claim 23, wherein the alloy has a resultant microstructure comprising M₂C carbide precipitates which measure less than 20 nm in the longest dimension.

25. The method of claim 24, wherein the M of the M₂C carbide precipitates comprises one or more elements selected from the group consisting of: Mo, Cr, W, and V.

20 26. The method of any one of claims 22 to 25, wherein the alloy comprises, in combination by weight, 0.25% to 0.31% carbon, 6.8% to 8.0% cobalt, 9.3 to 10.5% nickel, 0.8% to 2.6% chromium, 0.9% to 2.1% molybdenum, 0.7% to 2.0% tungsten, 0.05% to 0.12% vanadium, and up to 0.015% titanium, the balance iron and impurities.

27. The method of any one of claims 22 to 25, wherein the alloy comprises, in 25 combination by weight, 0.29% to 0.31% carbon, 6.8% to 7.2% cobalt, 9.8 to 10.2% nickel,

61368-1359(S)

16

0.8% to 2.6% chromium, 0.9% to 2.1% molybdenum, 0.7% to 1.4% tungsten, 0.05% to 0.12% vanadium, and up to 0.015% titanium, the balance iron and impurities.

28. The alloy according to claim 1 or 2, wherein the alloy comprises, by weight, 1.0% to 3.0% chromium,

5 wherein the alloy has a predominately lath martensite microstructure and is strengthened at least in part by M_2C carbide precipitates which measure less than 20 nm in the longest dimension, where M comprises one or more elements selected from the group consisting of Mo, Cr, W, and V, and

wherein the alloy has an ultimate tensile strength of at least 1900 MPa and a
10 K_{IC} fracture toughness of at least 110 MPa \sqrt{m} .

29. A method for processing a steel alloy, the method comprising:

providing a steel alloy comprising, in combination by weight, 0.20% to 0.33% carbon, 4.0% to 8.0% cobalt, 7.0 to 11.0% nickel, 0.8% to 3.0% chromium, 0.5% to 2.5% molybdenum, 0.5% to 5.9% tungsten, 0.05% to 0.20% vanadium, and up to 0.02% titanium,
15 the balance essentially iron and incidental elements and impurities;

subjecting the alloy to a solutionizing heat treatment at 950°C to 1100°C for 60-90 minutes; and

subjecting the alloy to a tempering heat treatment at 465°C to 550°C for 4-32 hours;

20 wherein the non-stainless steel alloy further includes Ti-enriched carbides, and the alloy is strengthened at least in part by M_2C carbide precipitates which measure less than 20 nm in the longest dimension.

30. The method of claim 29, wherein the steel alloy further comprises up to about 0.02% titanium.

61368-1359(S)

17

31. The method of claim 30, wherein the alloy comprises, in combination by weight, 0.25% to 0.31% carbon, 6.8% to 8.0% cobalt, 9.3 to 10.5% nickel, 0.8% to 2.6% chromium, 0.9% to 2.1% molybdenum, 0.7% to 2.0% tungsten, 0.05% to 0.12% vanadium, and up to 0.015% titanium, the balance essentially iron and incidental elements and

5 impurities.

32. The method of claim 30, wherein the alloy comprises, in combination by weight, 0.29% to 0.31% carbon, 6.8% to 7.2% cobalt, 9.8 to 10.2% nickel, 0.8% to 2.6% chromium, 0.9% to 2.1% molybdenum, 0.7% to 1.4% tungsten, 0.05% to 0.12% vanadium, and up to 0.015% titanium, the balance essentially iron and incidental elements and

10 impurities.

33. The method of claim 29 or 30, further comprising:

quenching the alloy after the solutionizing heat treatment; and

air cooling the alloy after the tempering heat treatment.

34. The method of claim 29 or 30, further comprising:

15 subjecting the alloy to a cryogenic treatment between the solutionizing heat treatment and the tempering heat treatment.

35. The method of claim 29 or 30, wherein the alloy has a resultant predominately lath martensite microstructure.

36. The method of claim 29 or 30, wherein the M of the M₂C carbide precipitates 20 comprises one or more elements selected from the group consisting of: Mo, Cr, W, and V.

37. A non-stainless steel alloy comprising, in combination by weight:

0.20% to 0.33% carbon, 4.0% to 8.0% cobalt, 7.0 to 11.0% nickel, 1.0% to 3.0% chromium, 0.5% to 2.5% molybdenum, 0.5% to 5.9% tungsten, 0.05% to 0.20%

61368-1359(S)

18

vanadium, and titanium, wherein the amount of titanium is more than 0, less than or equal to 0.02wt% of the alloy, the balance essentially iron and incidental elements and impurities,

wherein the alloy has a predominately lath martensite microstructure and is strengthened at least in part by M_2C carbide precipitates which measure less than 20 nm in the 5 longest dimension, where M comprises one or more elements selected from the group consisting of: Mo, Cr, W, and V, and

wherein the alloy has an ultimate tensile strength of at least 1900 MPa and a K_{IC} fracture toughness of at least $110 \text{ MPam}^{1/2}$;

wherein the non-stainless steel alloy further includes Ti-enriched carbides.

10 38. The alloy of claim 37, further comprising up to about 0.02% titanium.

39. The alloy of claim 38, wherein the alloy comprises, in combination by weight: 0.25% to 0.31% carbon, 6.8% to 8.0% cobalt, 9.3 to 10.5% nickel, 0.8% to 2.6% chromium, 0.9% to 2.1% molybdenum, 0.7% to 2.0% tungsten, 0.05% to 0.12% vanadium, and titanium, wherein the amount of titanium is more than 0, less than or equal to 0.015wt% of the alloy, 15 the balance essentially iron and incidental elements and impurities.

40. The alloy of claim 38, wherein the alloy comprises, in combination by weight: 0.29% to 0.31% carbon, 6.8% to 7.2% cobalt, 9.8 to 10.2% nickel, 0.8% to 2.6% chromium, 0.9% to 2.1% molybdenum, 0.7% to 1.4% tungsten, 0.05% to 0.12% vanadium, and titanium, wherein the amount of titanium is more than 0, less than or equal to 0.015wt% of the alloy, 20 the balance essentially iron and incidental elements and impurities.

41. A non-stainless steel alloy comprising, in combination by weight: about 0.20% to about 0.33% carbon, about 4.0% to about 8.0% cobalt, about 7.0 to about 11.0% nickel, about 0.8% about 3.0% chromium, about 0.5% to about 2.5% molybdenum, about 0.5% to about 5.9% tungsten, and about 0.05% to about 0.20% vanadium, 25 the balance essentially iron and incidental elements and impurities having a microstructure

61368-1359(S)

19

characterized by M_2C grain refinement particles wherein M_2 is comprised of Ti and by inclusion of principally M_2C carbide particle precipitates wherein M_2 is comprised of chromium (Cr), molybdenum (Mo), tungsten (W), and vanadium (V) and in a predominately lath martensite cobalt-nickel (Co, Ni) matrix, said alloy further characterized by a

5 combination of high strength and high fracture toughness (K_{ISCC}).

42. The alloy of claim 41, further comprising up to about 0.02% titanium.

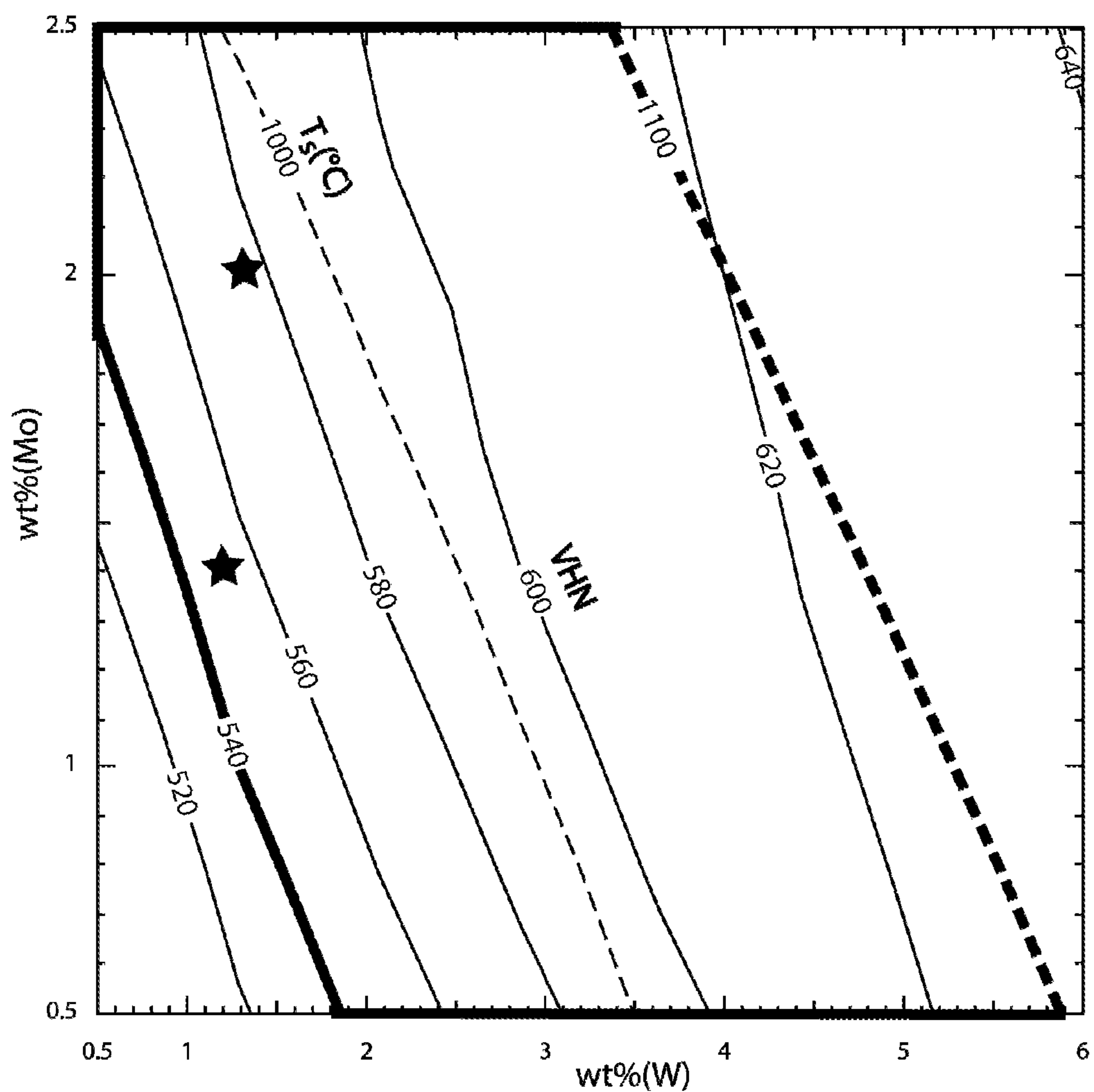
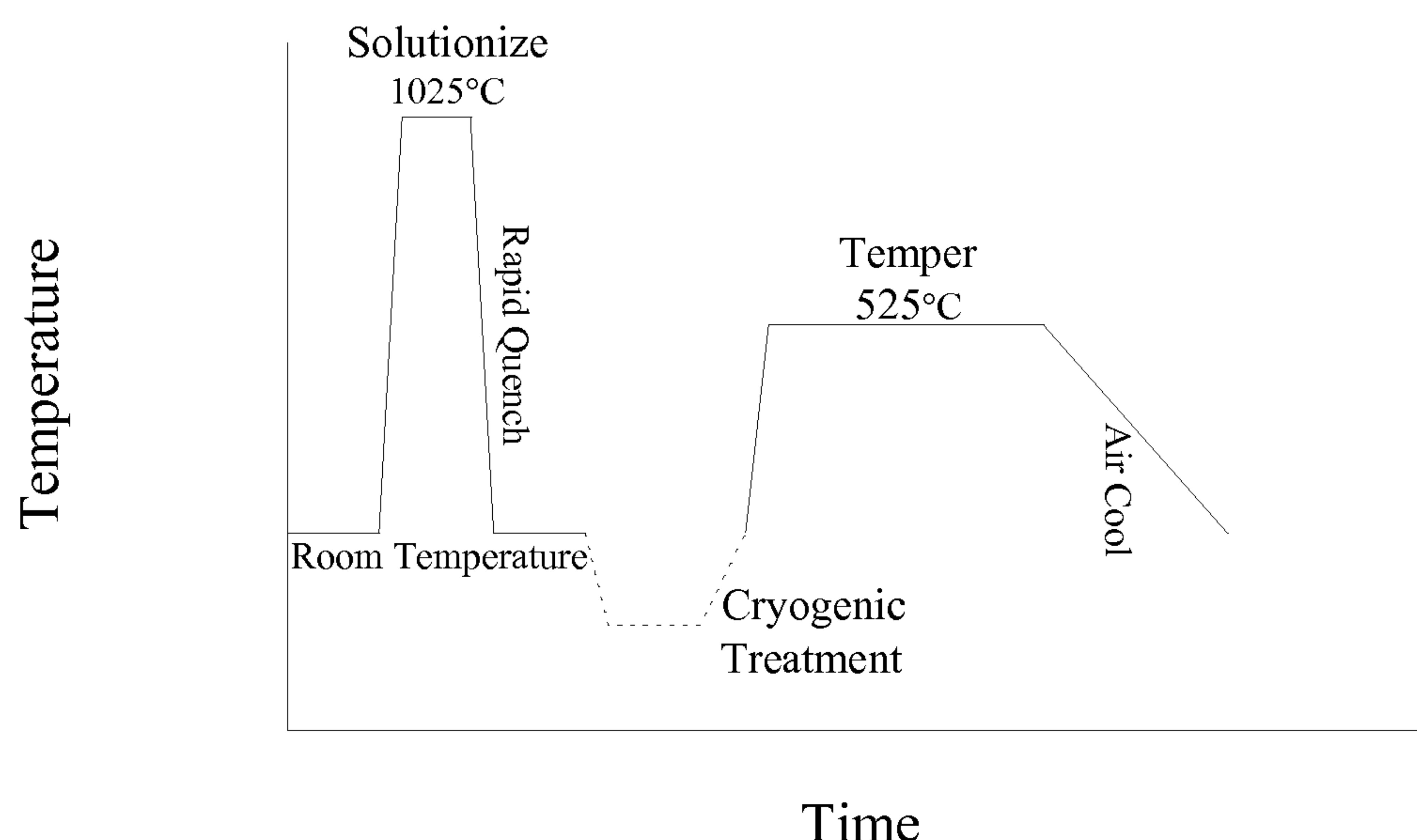


FIG. 1

**FIG. 2**

3/5

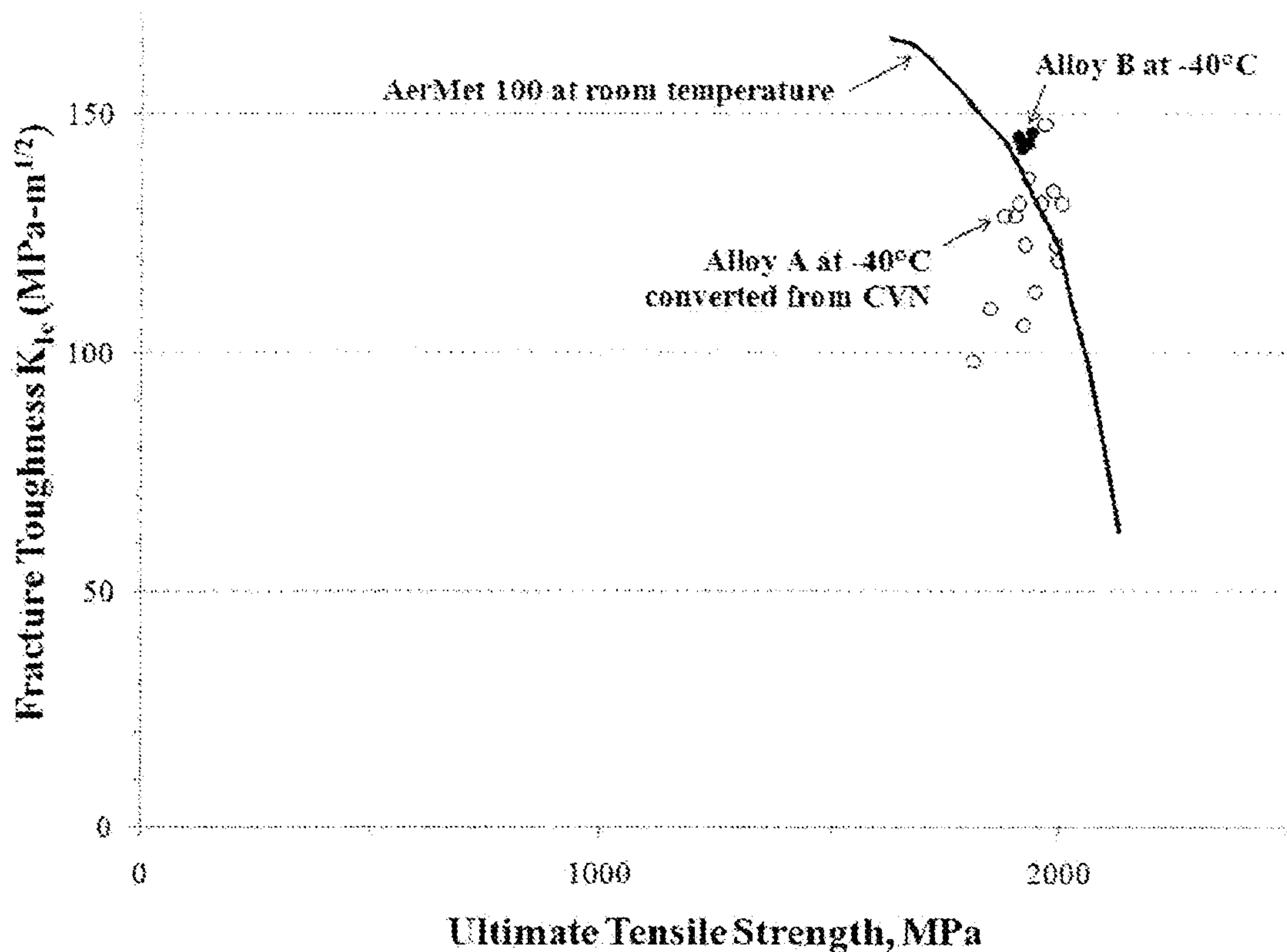


FIG. 3

4/5

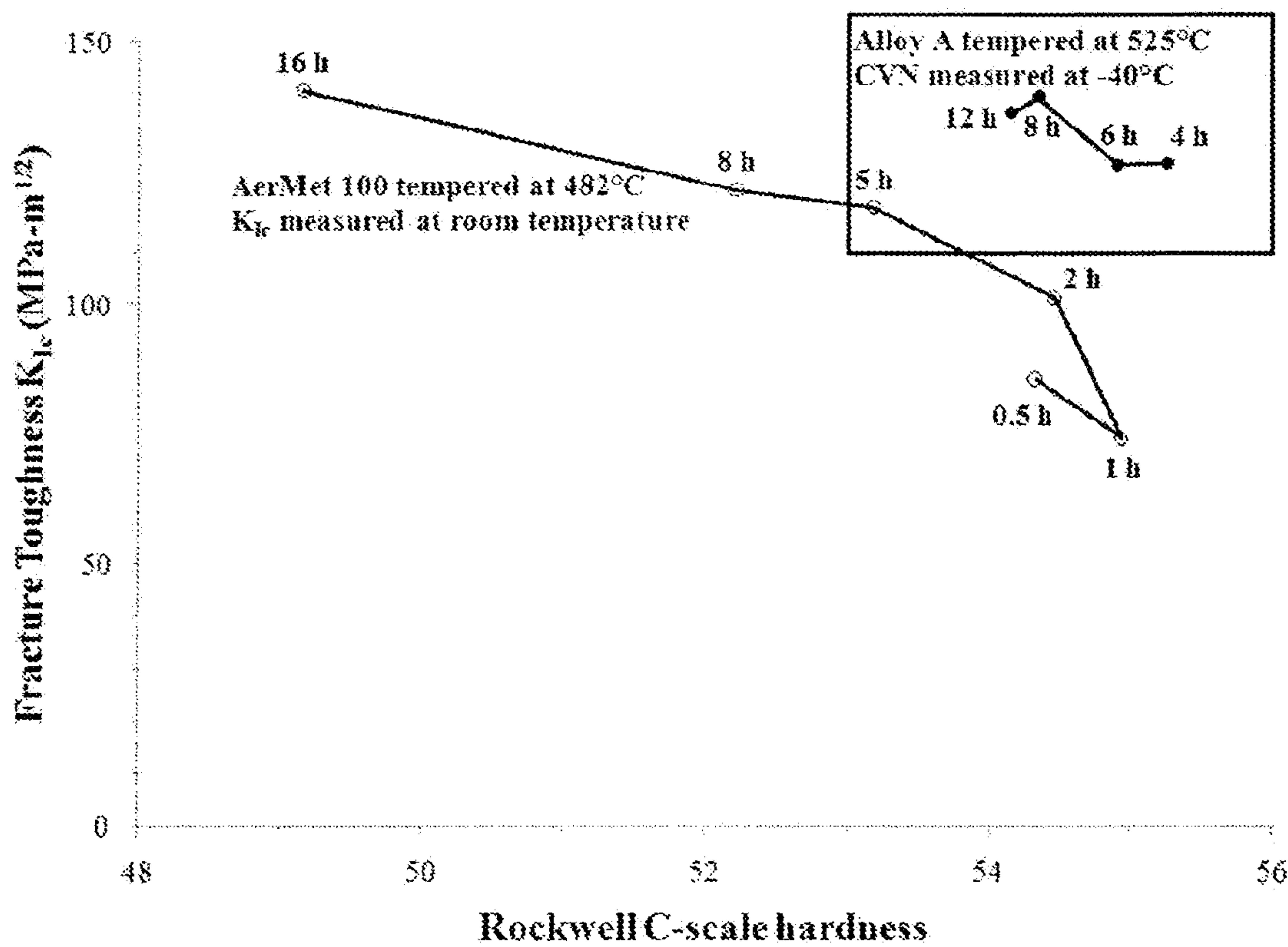


FIG. 4

5/5

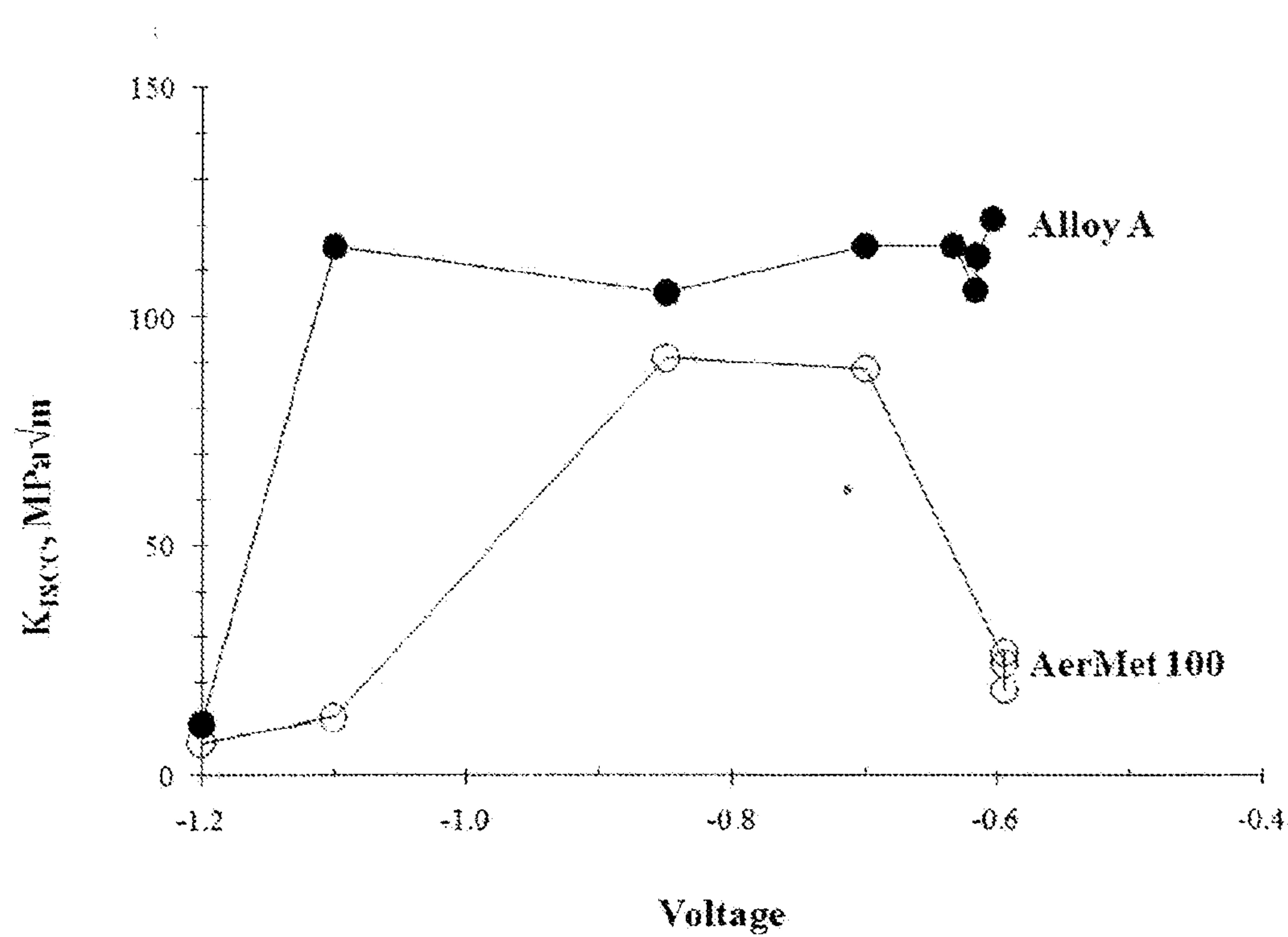


FIG. 5

Temperature

Solutionize

1025°C

Rapid Quench

Room Temperature

Temper

525°C

Air Cool

Cryogenic
Treatment

Time

FIG. 2