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(54) Title: LOW-CARBON, HIGH-STRENGTH 9% NICKEL STEELS FOR CRYOGENIC APPLICATIONS

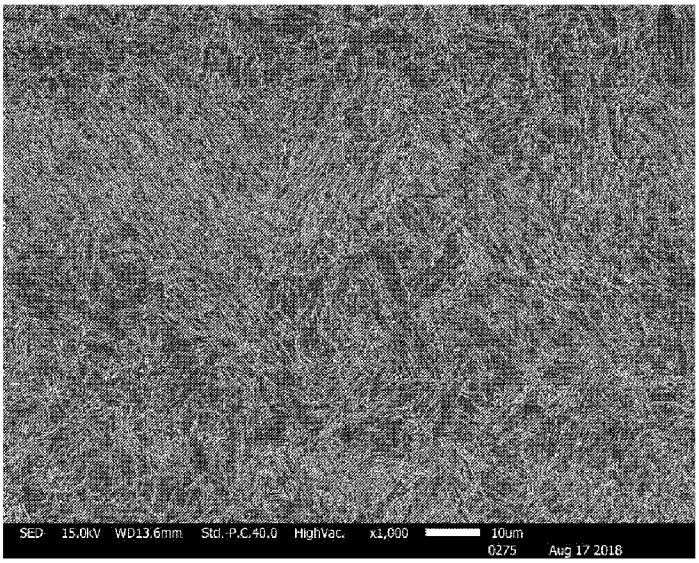


Figure 1

(57) Abstract: An ASTM A553 Type 1 cryogenic steel alloy comprising in wt.%: C: 0.01 - 0.04; Mn: up tp 2.0; P: up to 0.02; S: up to 0.15; Si: up to 1.0; Ni: 7 - 11; Cr: up to 1.0; Mo: up to 0.75; V: up to 0.2; Nb: up to 0.1; Al: up to 0.1; and N: up to 0.01. The cryogenic steel alloy may have an ultimate tensile strength of at least 900 MPa, a total elongation of at least 20%; a microstructure comprised of between 5 and 20 area % reverted austenite and the remainder tempered martensite; a transverse Charpy impact energy of at least 27 J at -196 °C; and a lateral expansion of at least 0.381 mm at -196 °C.

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Low-Carbon, High-Strength 9% Nickel Steels for Cryogenic Applications

Field of the Invention

The present invention relates to cryogenic steels, more specifically to ASTM A553 cryogenic steels. Most specifically, the invention relates to 9% Ni cryogenic steels that meet all the mechanical specifications of ASTM A553 alloys and have significantly higher ultimate tensile strengths than present ASTM A553 alloys.

Background of the Invention

For decades, the steel of choice for many cryogenic service conditions and reliable construction of cryogenic pressure vessels has been ASTM A553 (herein also 9%Ni steel). This steel has a tensile strength of 690 MPa and is impact tested at -196 °C. This 9% nickel steel was originally developed by the International Nickel Company. It generally has been used for construction of storage vessels for fluids such as liquid natural gas at cryogenic temperatures. While these steels have performed excellently in service, in recent years there has been interest in developing lower cost solutions for cryogenic storage.

Various steel producers have introduced new materials intended as direct substitutions for this grade. These materials are designed to achieve the strength and toughness requirements of ASTM A553 while benefiting from lower alloying cost. This provides the tank designer the opportunity to reduce tank construction cost while simultaneously meeting function and safety criteria.

The present inventors determined that rather than reducing the quantity of expensive alloying ingredients, enhancing the properties of the cryogenic steel would allow less steel to be used in the construction of such cryogenic tanks, by reducing the steel thickness needed for vessel fabrication. This would allow for the customer to order less material with the added benefit of lower vessel weight. Thus, there is a need in the art for a new steel that has higher strength than the present ASTM A553 alloys, and yet meets the Charpy impact energy absorption requirements of the ASTM A553 specification (minimum ASTM requirement of 27 J TCVN at -196 °C).

Summary of the Invention

The present invention is an ASTM A553 cryogenic steel alloy having lower C, and additions of Mo and V compared to prior art 9%Ni steels, while having significantly higher ultimate tensile strength. The alloy comprises in wt.%: C: 0.01 - 0.06; Mn: up to 2.0; P: up to 0.02; S: up to 0.15; Si: up to 1.0; Ni: 7 - 11; Cr: up to 1.0; Mo: up to 0.75; V: up to 0.2; Nb: up to 0.1; Al: up to 0.1; and N: up to 0.01. The cryogenic steel alloy may have an ultimate tensile strength of at least 900 MPa, a total elongation of at least 20%; a microstructure comprised of between 5 and 20 area % reverted austenite and the remainder tempered martensite; a transverse Charpy impact energy of at least 27 J at -196 °C; and a lateral expansion of at least 0.381 mm at -196 °C.

The cryogenic steel alloy may more preferably comprise in wt.%: C: 0.04 - 0.06; Mn: 0.5 - 0.7; Si: 0.2 - 0.4; Ni: 7.5 - 9.5; Cr: 0.25 - 0.5; Mo: 0.5 - 0.7; P: up to 0.006; S: up to 0.002; V: up to 0.1; Nb: up to 0.05; Al: up to 0.06 wt.%; and N: up to 0.008 wt.%.

The cryogenic steel alloy may have undergone a heat treatment comprising: austenitizing at a temperature of between 750 - 1000 °C for 10 minutes to 3 hours; quenching to room temperature; lamellarizing at a temperature of between 600 – 725 °C for 10 minutes to 3 hours; cooling to room temperature in air; tempering at a temperature of between 500 – 620 °C for 10 minutes to 3 hours; and cooling to room temperature in air.

More preferably, the austenitization is at a temperature of between 800 - 950 °C for 30 to 60 minutes; the lamellarizing is at a temperature of between 625 and 700 °C for 30 to 60 minutes; and the tempering is at a temperature of 550 and 610 °C for 30 to 60 minutes.

Most preferably, the austenitizing is at a temperature of between 820 - 900 °C for 30 to 60 minutes; the lamellarizing is at a temperature of between 650 and 675 °C for 30 to 60 minutes; and the tempering is at a temperature of 575 and 600 °C for 30 to 60 minutes.

The alloy microstructure may preferably contain between 8 and 15 area % reverted austenite and most preferably between 13 and 15 area % reverted austenite with the remainder tempered martensite.

The alloy may preferably have a lateral expansion of at least 1.0 mm at -196 °C, more preferably at least 1.5 mm and most preferably at least 2.0 mm. The alloy may also have a transverse Charpy impact energy of at least 50 J at -196 °C, more preferably at least 100 J, and most preferably at least 150 J.

Brief Description of the Drawings

Figure 1 is an SEM micrograph of an alloy of the present invention.

Detailed Description of the Invention

ASTM A553 Type I steel, commonly known as "9% Ni Steel," has requirements of a transverse Charpy absorbed energy of at least 27 J at -196 °C, a lateral expansion of at least 0.381 mm at -196 °C, and a total elongation of at least 20%. The A553 alloy must also have an ultimate tensile strength of at least 690 MPa. The inventive alloy meets all the mechanical requirements of the A553 alloy and has an ultimate tensile strength of at least 900 MPa.

The steel is heat treated by austenitizing/quenching, lamellarizing, and tempering. The resulting microstructure consists of predominantly martensite with significant volume fraction of reverted austenite plus carbides. The Charpy impact energy absorption of plates of the inventive steel are comparable with historic production values of ASTM A553 Type I despite the new steel exhibiting greater than 30 percent higher design strength. The broad compositional ranges of the inventive alloy are given in Table 1.

Table 1

	C	Mn	P	S	Si	Ni	Cr	Mo	V	Nb	Al	N
Min	0.01	0	0	0	0	7	0	0	0	0	0	0
Max	0.06	2	0.02	0.15	1	11	1	0.75	0.2	0.1	0.1	0.01

More preferred compositional ranges are given in Table 2

Table 2

	C	Mn	P	S	Si	Ni	Cr	Mo	V	Nb	Al	N
Min	0.04	0.5	0	0	0.2	7.5	0.25	0.5	0	0	0	0
Max	0.06	0.7	0.006	0.002	0.4	9.5	0.5	0.7	0.1	0.05	0.06	0.008

Plates 13 mm thick were formed of an alloy composition in Table 3.

Table 3

C	Mn	P	S	Si	Ni	Cr	Mo	V	Nb	Al	N
0.044	0.59	<0.005	<0.002	0.26	8.9	0.45	0.65	0.08	0.013	0.028	<0.005

The plates were austenitized at 843 °C for 15 minutes and immediately water quenched. The broad austenitization temperature range for the alloys of the present invention is between 750 - 1000 °C, more preferably between 800 - 950 °C and most preferably between 820 - 900 °C. The broad austenitization time range is between 10 minutes and 3 hours, most preferably the austenitization time is 30 to 60 minutes.

After austenization and quenching the plates were “lamellarized and tempered.” This is a two-step tempering process where the plate is lamellarized for a fixed time and temperature, air cooled to room temperature, and subsequently tempered for a fixed time and temperature and again air cooled to room temperature. The plates were lamellarized at 660 °C for 50 minutes. The broad lamellarization temperature range for the alloys of the present invention is between 600 – 725 °C, more preferably between 625 and 700 °C, and most preferably between 650 and 675 °C. The broad lamellarization time range is between 10 minutes and 3 hours, most preferably the lamellarization time range is between 30 to 60 minutes.

The plates were tempered at 590 °C for 25 minutes. The broad tempering temperature range for the alloys of the present invention is between 500 – 620 °C, more preferably between 550 and 610 °C, and most preferably between 575 and 600 °C. The

broad tempering time range is between 10 minutes and 3 hours, most preferably the tempering time range is between 30 to 60 minutes.

Figure 1 is an SEM micrograph of an alloy of the present invention which shows the microstructure thereof after austenitizing/quenching, lamellarizing, and tempering. The microstructure of the alloys is tempered martensite with interlath austenite containing lamellae. The presence of retained austenite was confirmed by x-ray diffraction. The percentage of retained austenite as well as the ultimate tensile strength (UTS) in MPa, yield strength (YS) in MPa, and total elongation % for samples of the inventive alloy are shown in Table 4. The broadest range of retained austenite in the inventive alloys is between 5 and 20%, more preferably between 8 and 15%, most preferably between 13 and 15%.

Table 4

Sample #	YS (MPa)	UTS (MPa)	Tot. El. (%)	% Retained Austenite
1	729	964	23.4	14.6
2	757	973	25.3	12.9
3	871	989	25.0	14.7

The tensile results in Table 4 demonstrate that the desired minimum tensile strength requirement of 900 MPa was achieved for all tested specimens. Table 4 also demonstrates that the minimum tensile elongation of 20% specified by the ASTM A553 requirements was achieved for all specimens.

Table 5 presents results for transverse Charpy impact energy at -196 °C in Joules and the lateral expansion at -196 °C in mm for samples of the instant inventive alloy. Clearly the alloy easily meets/exceeds the ATM A553 requirements. Thus, the

inventive alloy has a lateral expansion of at least 0.381 mm at -196 °C, preferably at least 1.0 mm, more preferably at least 1.5 mm and most preferably at least 2.0 mm. Also, the inventive alloy has a transverse Charpy impact energy of at least 27 J at -196 °C, preferably at least 50 J, more preferably at least 100 J and most preferably at least 150 J.

Table 5

Test #	TCVN @ -196 C (J)	Lat. Exp. @ -196 C (mm)
1	151	1.73
2	170	2.39
3	159	1.45
4	181	2.01
5	166	2.08

We claim:

1. A cryogenic steel alloy, said alloy comprising in wt.%:

C: 0.01 - 0.06; Mn: up to 2.0; P: up to 0.02; S: up to 0.15; Si: up to 1.0; Ni: 7 - 11; Cr: up to 1.0; Mo: up to 0.75; V: up to 0.2; Nb: up to 0.1; Al: up to 0.1; and N: up to 0.01;

said alloy having an ultimate tensile strength of at least 900 MPa, a total elongation of at least 20%; a microstructure comprised of between 5 and 20 area % reverted austenite and the remainder tempered martensite; a transverse Charpy impact energy of at least 27 J at -196 °C; and a lateral expansion of at least 0.381 mm at -196 °C.

2. The cryogenic steel alloy of claim 1, wherein C comprises 0.04 - 0.06 wt.%

3. The cryogenic steel alloy of claim 2, wherein Mn comprises 0.5 - 0.7 wt.%

4. The cryogenic steel alloy of claim 3, wherein Si comprises 0.2 - 0.4 wt.%

5. The cryogenic steel alloy of claim 4, wherein Ni comprises 7.5 - 9.5 wt.%

6. The cryogenic steel alloy of claim 5, wherein Cr comprises 0.25 - 0.5 wt.%

7. The cryogenic steel alloy of claim 6, wherein Mo comprises 0.5 - 0.7 wt.%

8. The cryogenic steel alloy of claim 7, wherein the alloy comprises P: up to 0.006 wt.%; S: up to 0.002 wt.%; V: up to 0.1 wt.%; Nb: up to 0.05 wt.%; Al: up to 0.06 wt.%; and N: up to 0.008 wt.%.

9. The cryogenic steel alloy of claim 1, wherein said alloy has undergone a heat treatment comprising:
austenitizing at a temperature of between 750 - 1000 °C for 10 minutes to 3 hours;
quenching to room temperature;
lamellarizing at a temperature of between 600 – 725 °C for 10 minutes to 3 hours;
cooling to room temperature in air;
tempering at a temperature of between 500 – 620 °C for 10 minutes to 3 hours; and
cooling to room temperature in air.

10. The cryogenic steel alloy of claim 9, wherein said austenitizing is at a temperature of between 800 - 950 °C for 30 to 60 minutes; said lamellarizing is at a temperature of between 625 and 700 °C for 30 to 60 minutes; and said tempering is at a temperature of 550 and 610 °C for 30 to 60 minutes.

11. The cryogenic steel alloy of claim 10, wherein said austenitizing is at a temperature of between 820 - 900 °C for 30 to 60 minutes; said lamellarizing is at a temperature of between 650 and 675 °C for 30 to 60 minutes; and said tempering is at a temperature of 575 and 600 °C for 30 to 60 minutes.

12. The cryogenic steel alloy of claim 1, wherein said alloy has a microstructure comprised of between 8 and 15 area % reverted austenite and the remainder tempered martensite.

13. The cryogenic steel alloy of claim 12, wherein said alloy has a microstructure comprised of between 13 and 15 area % reverted austenite and the remainder tempered martensite.

14. The cryogenic steel alloy of claim 1, wherein said alloy has a lateral expansion of at least 1.0 mm at -196 °C.

15. The cryogenic steel alloy of claim 14, wherein said alloy has a lateral expansion of at least 1.5 mm at -196 °C.

16. The cryogenic steel alloy of claim 14, wherein said alloy has a lateral expansion of at least 2.0 mm at -196 °C.

17. The cryogenic steel alloy of claim 1, wherein said alloy has a transverse Charpy impact energy of at least 50 J at -196 °C.

18. The cryogenic steel alloy of claim 17, wherein said alloy has a transverse Charpy impact energy of at least 100 J at -196 °C.

19. The cryogenic steel alloy of claim 18, wherein said alloy has a transverse Charpy impact energy of at least 150 J at -196 °C.

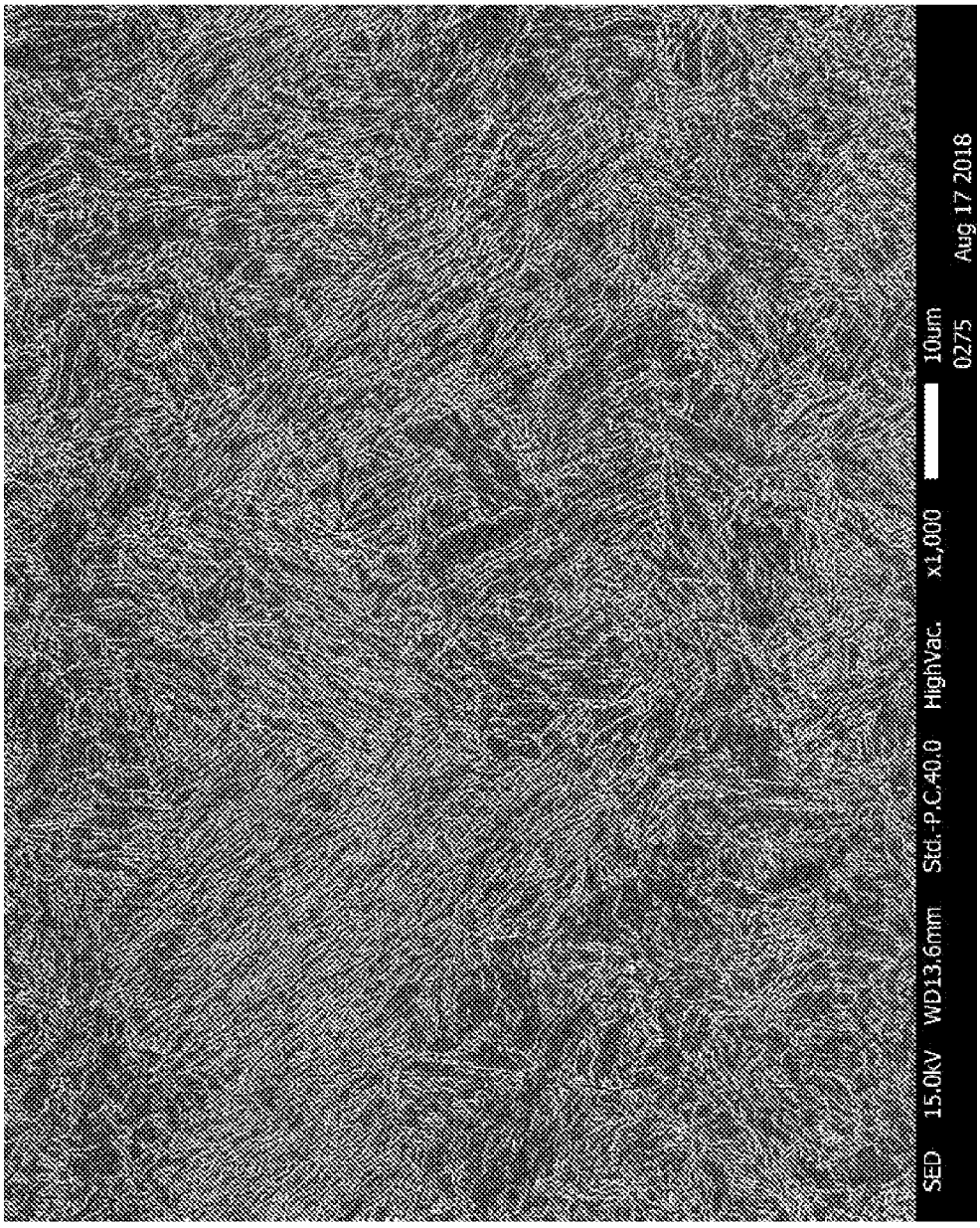

SED 15.0kV WD13.6mm Std.-P.C.40.0 HighVac. x1,000 10um
0275 Aug 17 2018

Figure 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2018/060323

A. CLASSIFICATION OF SUBJECT MATTER
INV. C21D6/00 C21D1/18 C21D1/22 C22C38/08 C22C38/12
C22C38/44 C22C38/46
ADD.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C21D C22C

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 619 302 A (AOKI KOICHI ET AL) 9 November 1971 (1971-11-09) claims 1-8; figure 1; example 9a; table 2 -----	1-19
X	US 4 776 900 A (YANO SEINOSUKE [JP] ET AL) 11 October 1988 (1988-10-11) claims 1-6; examples A1,A2; tables 1,2 -----	1-19
	-/--	

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2018/060323

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2018/060323

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	FR 2 307 879 A1 (SIDERURGIE FSE INST RECH [FR]) 12 November 1976 (1976-11-12) claims 1-7; example 1	1-19

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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