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(19) **United States**(12) **Patent Application Publication** (10) **Pub. No.: US 2006/0169368 A1**
Lopez et al. (43) **Pub. Date: Aug. 3, 2006**(54) **LOW CARBON ALLOY STEEL TUBE
HAVING ULTRA HIGH STRENGTH AND
EXCELLENT TOUGHNESS AT LOW
TEMPERATURE AND METHOD OF
MANUFACTURING THE SAME****Publication Classification**(51) **Int. Cl.**
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Liechtenstein Corporation)**(21) Appl. No.: **11/395,322**(22) Filed: **Apr. 3, 2006****Related U.S. Application Data**(63) Continuation-in-part of application No. 10/957,605,
filed on Oct. 5, 2004.(57) **ABSTRACT**

A low carbon alloy steel tube and a method of manufacturing the same, especially for a stored gas inflator pressure vessel, in which the steel tube consists essentially of, by weight: about 0.06% to about 0.18% carbon, about 0.3% to about 1.5% manganese, about 0.05% to about 0.5% silicon, up to about 0.015% sulfur, up to about 0.025% phosphorous, and at least one of the following elements: up to about 0.30% vanadium, up to about 0.10% aluminum, up to about 0.06% niobium, up to about 1% chromium, up to about 0.70% nickel, up to about 0.70% molybdenum, up to about 0.35% copper, up to about 0.15% residual elements, and the balance iron and incidental impurities. After a high heating rate of about 100° C. per second; rapidly and fully quenching the steel tubing in a water-based quenching solution at a cooling rate of about 100° C. per second. The steel has a tensile strength of at least about 145 ksi and as high as 220 ksi and exhibits ductile behavior at temperatures as low as -100° C.

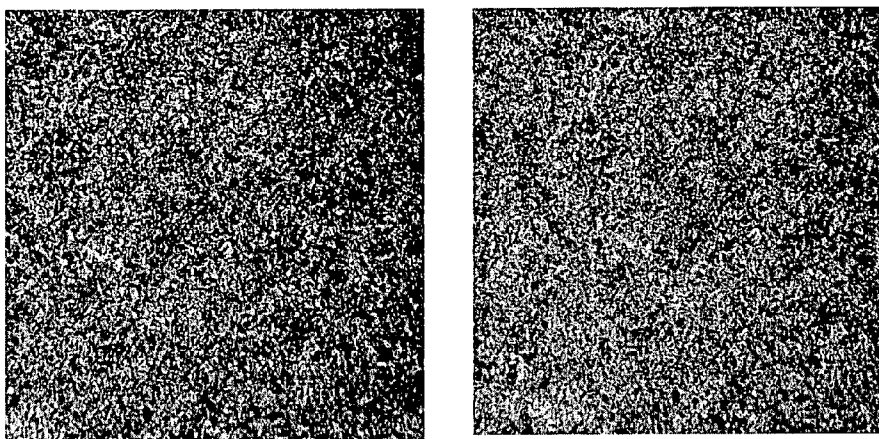


Figure I. High speed quenching, Steel E

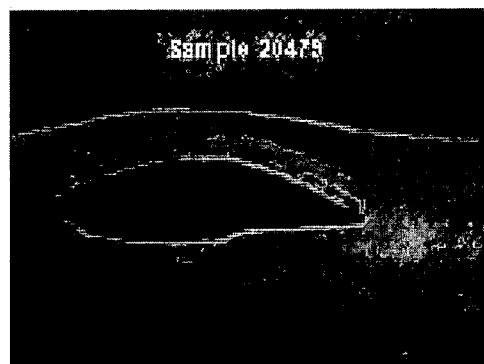


Figure II. Burst tests at -60°C for high speed quench Steel E. Ductile behavior

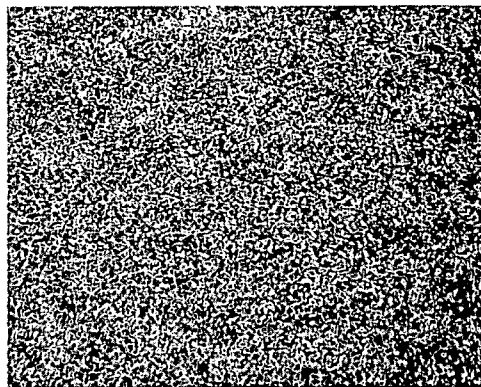
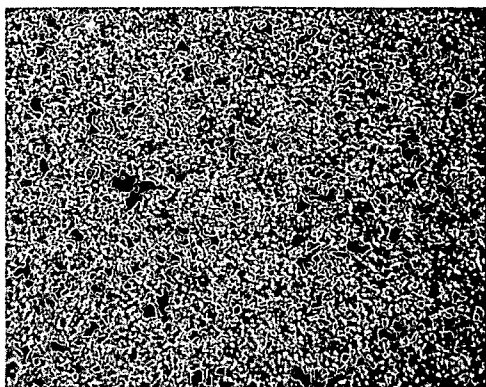


Figure III. Normal quenching Steel E

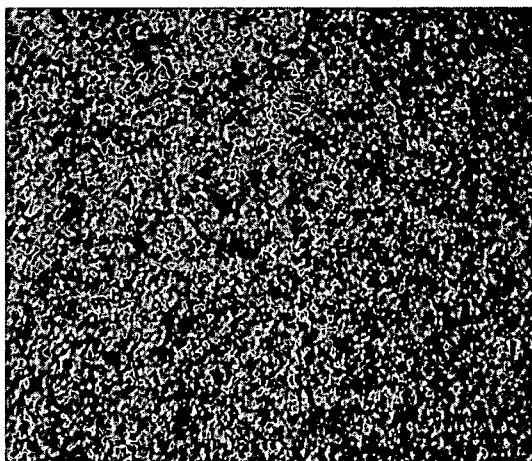


Figure IV. High speed quench Steel D.

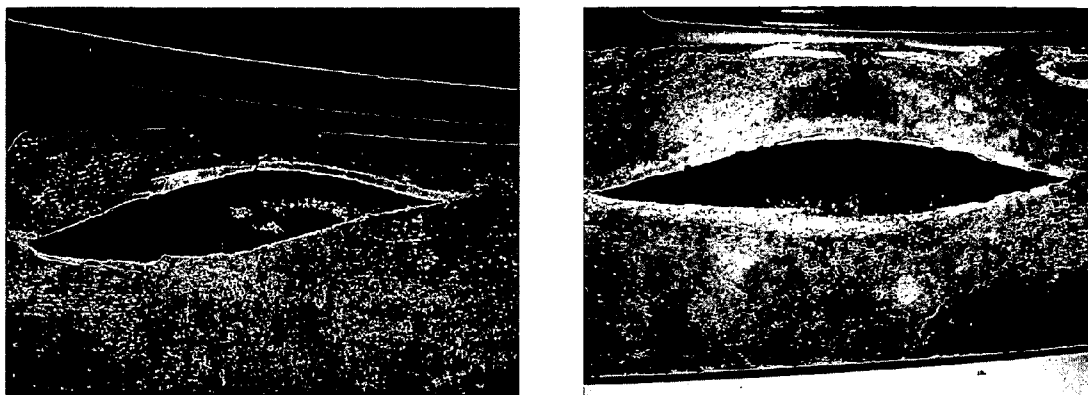


Figure V. Burst tests at -60°C for high speed quench Steel D. Ductile behavior

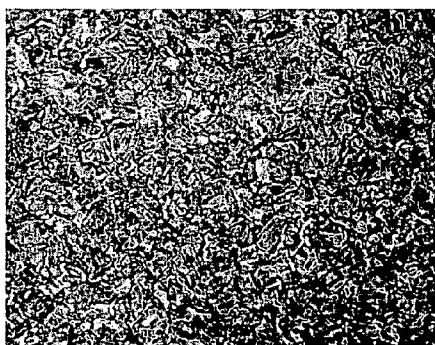


Figure VI. Micro-structure for normal quench Steel D.

**LOW CARBON ALLOY STEEL TUBE HAVING
ULTRA HIGH STRENGTH AND EXCELLENT
TOUGHNESS AT LOW TEMPERATURE AND
METHOD OF MANUFACTURING THE SAME**

RELATED APPLICATION

[0001] This application is a Continuation-in-part of U.S. Nonprovisional patent application Ser. No. 10/957,605, filed on Oct. 5, 2004.

BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] The present invention relates to low carbon alloy steel tubes having ultra high strength and excellent toughness at low temperature and also to a method of manufacturing such a steel tube. The steel tube is particularly suitable for making components for containers for automotive restraint systems, an example of which is an automotive airbag inflator.

[0004] In addition, alternative steel compositions in the low carbon, low alloy category and different heat treatment processes were developed and tested in order to decrease the manufacturing cost.

[0005] 2. Brief Description of the Prior Art

[0006] Japanese Publication No. 10-140249 [Application date Nov. 5, 1996] and Japanese Publication No. 10-140283 [Application date Nov. 12, 1996] illustrate in general terms steel chemistry considered useful for an automotive airbag inflator. These documents mention as a final condition the absence of heat treatment, a stress relieving, and a normalizing or a quenching and tempering. These publications do not mention the possibility of just a quenching as a heat treatment step. No mechanical properties are mentioned in the claims. In the various examples, only in example #21 is the steel quenched and tempered, but the reported UTS is only 686 MPa (99 ksi). Even the highest stated mechanical properties, in example #26, are relatively low, with a maximum UTS of 863 MPa (125 ksi). Hence, these publications relate to grades which are relatively low (the intended target is 590 MPa (86 ksi)). In addition these publications show ductility at low temperature with a flattening drop-weight (DW) type test at -40° C. The currently accepted test for demonstrating ductility at low temperature is the burst test, which is more efficient in showing brittleness. It is believed that most of the examples shown in these documents that are alleged to be ductile after a DW test, would in fact not show ductile behavior at low temperature in a burst test and, therefore, would not qualify for certain airbag inflator applications due to a lack of compliance with governmental regulations (e.g. US DOT).

[0007] Japanese Publication No. 2001-49343 [Application date Oct. 8, 1999] is said to address only steels for use in making electric-resistance-welded tubes (the ERW process). The claims specify various aspects of the ERW process and an optional heat treatment for a normalizing or quench and temper, an optional ulterior cold drawing, an optional ulterior heat treatment (normalizing or quench and temper). This document addresses only two different, very general steel chemistry, one being a low carbon steel, the other noting common limits in various alloying elements. This document does not suggest the possibility of just a quenching heat

treatment. Various examples are given for a quench and temper material, but mechanical properties obtained are relatively low. The maximum result achieved is 852 MPa (123 ksi) in the quench and temper test #18.

[0008] It is believed that the steel "chemistry" put forth by Sumitomo in each of JP 10-140249 JP 10-140283; JP 2001-49343; as well as the chemistry later identified in Kondo et al., U.S. Pat. No. 6,878,219 B2, or the continuation published as US 2005/0039826 A1, actually define steels with such broad ranges so as to include SAE 1010 general purpose steel as made and sold in the US since long prior to 1990. Applicants are aware that for several years a SAE 1010 steel grade manufactured with modern technologies normally guarantees that a P amount will be below 0.025 and an S amount will be below 0.01 as described in the mentioned application.

[0009] Additional documents illustrating the state of the prior art in steels for air bag applications include Erike, U.S. Pat. No. 6,386,583 B2 and various published continuations thereof, including US 2004/0074570 A1 and US 2005/0061404 A1. These documents do not suggest any advantage as taught herein from an extremely rapid induction austenitizing and an ulterior ultra fast water quenching, let alone using just such a rapid quench and not thereafter using a tempering step. In addition JP 10-140283 discloses overlapping chemistry with U.S. Pat. No. 6,878,219 B2, with only a slightly lower maximum for P (0.02) and a slightly higher maximum for S (0.02). While Patent Publication US20020033591A1 broadly suggests the possibility of quenching without tempering, claims 6 and 7 do not mention the necessity of quenching in order to achieve the mechanical properties claimed and instead these claims require at least two heat treatments.

[0010] Airbag inflators for vehicle occupant restraint systems are required to meet strict structural and functional standards. Therefore, strict procedures and tolerances are imposed on the manufacturing process. While field experience indicates that the industry has been successful in meeting past structural and functional standards, improved and/or new properties are necessary to satisfy the evolving requirements, while at the same time a continuous reduction in the manufacturing costs is also important.

[0011] Airbags or supplemental restraint systems are an important safety feature in many of today's vehicles. In the past, air bag systems were of the type employing explosive chemicals, but they are expensive, and due to environmental and recycling problems, in recent years, a new type of inflator has been developed using an accumulator made of a steel tube filled with argon gas or the like, and this type is increasingly being used.

[0012] The above-mentioned accumulator is a container which at normal times maintains the gas or the like at a high pressure which is blown into an airbag at the time of the collision of an automobile, in a single or multiple stage burst. Accordingly, a steel tube used as such an accumulator is to receive a stress at a high strain rate in an extremely short period of time. Therefore, compared with a simple structure such as an ordinary pressure cylinder, the above-described steel tube is required to have superior dimensional accuracy, excellent workability, and weldability, and above all must have high strength, toughness, and excellent resistance to bursting. Dimensional accuracy also is important to ensure a very precise volume of gas will blow into the airbag.

[0013] Cold forming properties are very important in tubular members used to manufacture accumulators since they are formed to final shape after the tube is manufactured.

[0014] Different shapes depending on the vessel configuration shall be obtained by cold forming. It is crucial to obtain pressure vessels without cracks and superficial defects after cold forming. Moreover, it is also vital to have very good toughness even at low temperatures after cold forming.

[0015] The steels disclosed herein have very good weldability, and do not require, for air bag accumulator applications, either a preheating prior to welding, or a post weld heat treatment. The carbon equivalent, as defined by the formula,

$$Ceq = \% C + \% Mn/6 + (\% Cr + \% Mo + \% V)/5 + (\% Ni + \% Cu)/15$$

should be less than about 0.63% in order to obtain the required weldability. As Ceq diminishes, weldability improves. In the preferred embodiment of this invention, the carbon equivalent as defined above should be less than about 0.60%, preferably less than about 0.56%, and most preferably less than about 0.52%, or even less than about 0.48%, in order to better guarantee weldability.

[0016] To produce a gas container, a cold-drawn tube made according to the present invention is cut to length and then cold formed using different known technologies (such as crimping, swaging, or the like) in order to obtain the desired shape. Alternatively, a welded tube could be used. Subsequently, to produce the accumulator, an end cap and a diffuser are welded to each end of the container by any suitable technology such as friction welding, gas tungsten arc welding or laser welding. These welds are highly critical and as such require considerable labor, and in certain instances testing to assure weld integrity throughout the pressure vessel and airbag deployment. It has been observed that these welds can crack or fail, thus, risking the integrity of the accumulator, and possibly the operation of the airbag.

[0017] The inflators are tested to assure that they retain their structural integrity during airbag deployment. One of such tests is the so-called burst test. This is a destructive-type test in which a canister is subjected to internal pressures significantly higher than those expected during normal operational use, i.e., airbag deployment. In this test, the inflator is subjected to increasing internal pressures until rupture occurs.

[0018] In reviewing the burst test results and studying the test canister specimens from these tests, it has been found that fracture occurs through different alternative ways: ductile fracture, brittle fracture, and sometimes a combination of these two modes. It has been observed that in ductile fracture an outturned rupture exemplified by an opened bulge (such as would be exhibited by a bursting bubble) occurs. The ruptured surface is inclined approximately 45 degrees with respect to the tube outer surface, and is localized within a subject area. In a brittle fracture, on the other hand, a non-arresting longitudinal crack along the length of the inflator is exhibited, which is indicative of a brittle zone in the material. In this case, the fracture surface is normal to the tube outer surface. These two modes of fracture have distinctive surfaces when observed under a scanning electron microscope—dimples are characteristic of ductile fracture, while cleavage is an indication of brittleness.

[0019] At times, a combination of these two fracture modes can be observed, and brittle cracks can propagate from the ductile, ruptured area. Because the whole system, including the airbag inflator, may be utilized in vehicles operating in very different climates, it is crucial that the material exhibits ductile behavior over a wide temperature range, from very cold up to warm temperatures.

SUMMARY OF THE INVENTION

[0020] First, the present invention first relates to certain novel low carbon alloy steels suitable for cold forming having more than high tensile strength (UTS 145 ksi minimum) and preferably ultra high tensile strength (UTS 160 ksi minimum and possibly 175 ksi or 220 ksi), and, consequently, a very high burst pressure. Moreover, the steel has excellent toughness at low temperature, with guaranteed ductile behavior at -60°C ., i.e., a ductile-to-brittle transition temperature (DBTT) below 60°C ., and possibly as low as -100°C .

[0021] Second, the present invention also relates to a process of manufacturing such a steel tube which essentially comprises a novel rapid induction austenizing/high speed quench/no temper technique. In a preferred method, there is an extremely rapid induction austenizing with an ultra fast water quenching step that eliminates any tempering step, so as to create a low carbon alloy steel tube that also is suitable for cold forming having ultra high tensile strength (UTS 145 ksi minimum and up to 220 ksi), and, consequently, a very high burst pressure. Moreover, the steel has excellent toughness at low temperature, with guaranteed ductile behavior at -60°C ., i.e., a ductile-to-brittle transition temperature (DBTT) that is below -60°C ., and possibly even as low as -100°C .

[0022] The material of the present invention has particular utility in components for containers for automotive restraint system components, an example of which is an automotive airbag inflator. The chemistry used to create each of the steels disclosed herein is novel, hereafter will be identified as Steel A, Steel B, Steel C, Steel D and Steel E, with the compositions for each being summarized in the following Table I:

Steel	C	Mn	S	P	Cr	Mo	Ni	V
A	0.10	1.23	0.002	0.008	0.11	0.05	0.34	0.002
B	0.10	1.09	0.001	0.011	0.68	0.41	0.03	0.038
C	0.11	1.16	0.001	0.010	0.64	0.47	0.03	0.053
D	0.11	1.07	0.002	0.008	0.06	0.04	0.03	0.083
E	0.10	0.47	0.001	0.011	0.04	0.02	0.05	0.001

Steel	Ti	Si	Cu	Al	Carbon. eq
A	0.023	0.27	0.24	0.035	0.38
B	0.025	0.28	0.22	0.035	0.52
C	0.026	0.25	0.22	0.028	0.55
D	0.001	0.08	0.06	0.033	0.33
E	0.002	0.19	0.07	0.027	0.20

[0023] Test results using each of these steels in a novel rapid induction austenizing/high speed quench/no temper technique revealed surprising and differing results, among the five steel compositions, as summarized in the following Table II:

Steel	Yield		UTS		Elong.	Hardness	Flatten	Burst	
	(MPa)	(ksi)	(MPa)	(ksi)				−60° C.	−100° C.
A	920	133	1230	178	22	42	OK	ductile	ductile
B	940	136	1217	176	22	41	OK	ductile	N/A
C	997	144	1260	183	20	42	OK	ductile	N/A
D	781	113	1184	172	19	32	OK	ductile	N/A
E	552	80	827	120	26	17	OK	ductile	N/A

BRIEF DESCRIPTION OF THE DRAWINGS

[0024] Preferred embodiments of the invention are described in detail below, by example only, with reference to the accompanying drawings, wherein:

[0025] FIG. I is a core microstructure for a high speed quench on Steel E;

[0026] FIG. II shows burst tests at −60 C for a high speed quench on Steel E.

[0027] FIG. III shows microstructure for a normal quench on Steel E;

[0028] FIG. IV shows a high speed quench core microstructure on Steel D;

[0029] FIG. V shows burst test at −60 C for a high speed quench on Steel D.

[0030] FIG. VI shows micro-structure for a normal quench on Steel D

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0031] While the present invention is susceptible of embodiment in various forms, it will hereinafter be described a presently preferred embodiment with the understanding that the present disclosure is to be considered an exemplification of the invention and is not intended to limit the invention to the specific embodiment illustrated.

[0032] The present invention relates to steel tubing to be used for stored gas inflator pressure vessels. More particularly, the present invention relates to a low carbon ultra high strength steel grade for seamless pressure vessel applications with guaranteed ductile behavior at −60° C., i.e., a ductile-to-brittle transition temperature below −60° C., and possibly even as low as −100°

[0033] More particularly, the present invention relates to a chemical composition and a manufacturing process to obtain a seamless steel tubing to be used to manufacture an inflator.

[0034] A schematic illustration of a method of producing the seamless low carbon ultra high strength steel could be as follows:

1. Steel making
2. Steel casting
3. Tube hot rolling
4. Hot-rolled hollow finishing operations
5. Cold drawing

6. Austenizing with Quenching (without tempering)

7. Cold-drawn tube finishing operations

[0035] One of the main objectives of the steel-making process is to refine the iron by removal of carbon, silicon, sulfur, phosphorous, and manganese. In particular, sulfur and phosphorous are prejudicial for the steel because they worsen the mechanical properties of the material. Ladle metallurgy is used before or after basic processing to perform specific purification steps that allow faster processing in the basic steel making operation.

[0036] The steel-making process is performed under an extreme clean practice in order to obtain a very low sulfur and phosphorous content, which in turn is crucial for obtaining the high toughness required by the product. Accordingly, the objective of an inclusion level of 2 or less—thin series—, and level 1 or less—heavy series—, under the guidelines of ASTM E45 Standard-Worst Field Method (Method A) has been imposed. In the preferred embodiment of this invention, the maximum microinclusion content as measured according to the above-mentioned Standard should be:

Inclusion Type	Thin	Heavy
A	0.5	0
B	1.5	1.0
C	0	0
D	1.5	0.5

[0037] Furthermore, the extreme clean practice allows obtaining oversize inclusion content with 30 μm or less in size. These inclusion contents are obtained limiting the total oxygen content to 20 ppm.

[0038] Extreme clean practice in secondary metallurgy is performed by bubbling inert gases in the ladle furnace to force the inclusion and impurities to float. The production of a fluid slag capable of absorbing impurities and inclusions, and the inclusions' size and shape modification by the addition of SiCa to the liquid steel, produce high quality steel with low inclusion content.

Examples Using Low Carbon, Alloy Steels

[0039] The chemical composition of the obtained steel shall be as follows, in each case “%” means “mass percent”:

Carbon (C)

[0040] C is an element that inexpensively raises the strength of the steel, but if its content is less than 0.06% it is difficult to obtain the desired strength. On the other hand, if the steel has a C content greater than 0.18%, then cold workability, weldability, and toughness decrease. Therefore, the C content range is 0.06% to 0.18%. A preferred range for the C content is 0.07% to 0.12%, and an even more preferred range is 0.10 to 0.12%.

Manganese (Mn)

[0041] Mn is an element which is effective in increasing the hardenability of the steel, and therefore it increases strength and toughness. If its content is less than 0.3% it is difficult to obtain the desired strength, whereas if it exceeds 1.5%, then banding structures become marked, and toughness decreases. Accordingly, the Mn content is 0.3% to 1.5%, with a preferred Mn range of 0.60 to 1.40%.

Silicon (Si)

[0042] Si is an element which has a deoxidizing effect during steel making process and also raises the strength of the steel. If Si content is less than 0.05%, the steel is susceptible to oxidation, on the other hand if it exceeds 0.50%, then both toughness and workability decrease. Therefore, the Si content is 0.05% to 0.5%, and a preferred Si range of 0.05% to 0.40%.

Sulfur (S)

[0043] S is an element that causes the toughness of the steel to decrease. Accordingly, the S content is limited to 0.015% maximum. A preferred maximum value is 0.010%.

Phosphorous (P)

[0044] P is an element that causes the toughness of the steel to decrease. Accordingly, the P content is limited to 0.025% maximum. A preferred maximum value is 0.02%,

Nickel (Ni)

[0045] Ni is an element that increases the strength and toughness of the steel, but it is very costly, therefore for cost reasons Ni is limited to 0.70% maximum. A preferred maximum value is 0.50%.

Chromium (Cr)

[0046] Cr is an element which is effective in increasing the strength, toughness, and corrosion resistance of the steel. If it exceeds 1% the toughness at the welding zones decreases markedly. Accordingly, the Cr content is limited to 1.0% maximum, and a preferred Cr maximum content is 0.80%,

Molybdenum (Mo)

[0047] Mo is an element which is effective in increasing the strength of the steel and contributes to retard the softening during tempering, but it is very costly. Accordingly, the Mo content is limited to 0.7% maximum, and a preferred Mo maximum content is 0.50%

Vanadium (V)

[0048] V is an element which is effective in increasing the strength of the steel, even if added in small amounts, and allows to retard the softening during tempering. However, this ferroalloy is expensive, forcing the necessity to lower

the maximum content. Therefore, V is limited to 0.3% maximum, with a preferred maximum of 0.20%

[0049] Preferred ranges for other elements not listed above are as follows:

Element	Weight %
Aluminum	0.10% max
Niobium	0.06% max
Sn	0.05% max
Sb	0.05% max
Pb	0.05% max
As	0.05% max

[0050] Residual elements in a single ladle of steel used to produce tubing or chambers shall be:

$$\text{Sn+Sb+Pb+As} \leq 0.15\% \text{ max, and}$$

$$\text{S+P} \leq 0.025$$

[0051] The next step is the steel casting to produce a solid steel bar capable of being pierced and rolled to form a seamless steel tube. The steel is cast in the steel shop into a round solid billet, having a uniform diameter along the steel axis.

[0052] The solid cylindrical billet of ultra high clean steel is heated to a temperature of about 1200° C. to 1300° C., and at this point undergoes the rolling mill process. Preferably, the billet is heated to a temperature of about 1250° C., and then passed through the rolling mill. The billet is pierced, preferably utilizing the known Manessmann process, and subsequently the outside diameter and wall thickness are substantially reduced while the length is substantially increased during hot rolling. For example, a 148 mm outside diameter solid bar is hot rolled into a 48.3 mm outside diameter hot-rolled tube, with a wall thickness of 3.25 mm.

[0053] The cross-sectional area reduction, measured as the ratio of the cross-sectional area of the solid billet to the cross-sectional area of the hot-rolled tube, is important in order to obtain a refined microstructure, necessary to get the desired mechanical properties. Therefore, the minimum cross-sectional area reduction is about 15:1, with preferred and most preferred minimum cross-sectional area reductions of about 20:1 and about 25:1, respectively.

[0054] The seamless hot-rolled tube of ultra high clean steel so manufactured is cooled to room temperature. The seamless hot-rolled tube of ultra high clean steel so manufactured has an approximately uniform wall thickness, both circumferentially around the tube and longitudinally along the tube axis.

[0055] The hot-rolled tube is then passed through different finishing steps, for example cut in length into 2 to 4 pieces, and its ends cropped, straightened at known rotary straightening equipment if necessary, and non-destructively tested by one or more of the different known techniques, like electromagnetic testing or ultrasound testing.

[0056] The surface of each piece of hot-rolled tube is then properly conditioned for cold drawing. This conditioning includes pickling by immersion in acid solution, and applying an appropriate layer of lubricants, like the known zinc phosphate and sodium estearate combination, or reactive

oil. After surface conditioning, the seamless tube is cold drawn, pulling it through an external die that has a diameter smaller than the outside diameter of the tube being drawn. In most cases, the internal surface of the tube is also supported by an internal mandrel anchored to one end of a rod, so that the mandrel remains close to the die during drawing. This drawing operation is performed without the necessity of previously heating the tube above room temperature.

[0057] The seamless tube is so cold drawn at least once, each pass reducing both the outside diameter and the wall thickness of the tube. The cold-drawn steel tube so manufactured has a uniform outside diameter along the tube axis, and a uniform wall thickness both circumferentially around the tube and longitudinally along the tube axis. The so cold-drawn tube has an outside diameter preferably between 10 and 70 mm, and a wall thickness preferably from 1 to 4 mm.

[0058] The cold-drawn tube is then heat treated in an austenizing furnace at a temperature of at least the upper austenizing temperature, or Ac3 (which, for the specific chemistry disclosed herein, is about 880° C.), but preferably above about 920° C. and below about 1050° C. This maximum austenizing temperature is imposed in order to avoid grain coarsening. This process can be performed either in a fuel furnace or in an induction-type furnace, but preferably in the latter. The transit time in the furnace is strongly dependent on the type of furnace utilized. It has been found that the high surface quality required by this application is better obtained if an induction type furnace is utilized. This is due to the nature of the induction process, in which very short transit times are involved, precluding oxidation to occur. Preferably, the austenizing heating rate is at least about 100° C. per second, but more preferably at least about 200° C. per second. The extremely high heating rate and, as a consequence, very low heating times, are important for obtaining a very fine grain microstructure, which in turn guarantees the required mechanical properties.

[0059] Furthermore, an appropriate filling factor, defined as the ratio of the round area defined by the outer diameter of the tube to the round area defined by the coil inside diameter of the induction furnace, is important for obtaining the required high heating rates. The minimum filling factor is about 0.16, and a preferred minimum filling factor is about 0.36.

[0060] At or close to the exit zone of the furnace the tube is quenched by means of an appropriate quenching fluid. The quenching fluid is preferably water or water-based quenching solution. The tube temperature drops rapidly to ambient temperature, preferably at a rate of at least about 100° C. per second, more preferably at a rate of at least about 200° C. per second. This extremely high cooling rate is crucial for obtaining a complete microstructure transformation.

[0061] In a technique where a tempering step is employed, the steel tube is then tempered with an appropriate temperature and cycle time, at a temperature below Ac1. Preferably, the tempering temperature is between about 400-600° C., and more preferably between about 450-550° C. Alternatively, the tempering temperature may be between 200° C. to 600° C. and more preferably between 250° C. to 550° C. The soaking time shall be long enough to guarantee a very good temperature homogeneity, but if it is too long, the desired

mechanical properties are not obtained. This tempering step is performed preferably in a protective reducing or neutral atmosphere to avoid decarburizing and/or oxidation of the tube.

[0062] In a preferred method, the tempering step is eliminated and only a high speed quench using water or water based solutions, as described above, is employed.

[0063] In order to achieve a high speed quench, the following equipment is preferred, but not required.

[0064] A Quenching line with a full capacity of 2200 kg per hour, follows an induction furnace with a maximum power of inductor settled at 500 Kw. A head quencher employs 42 lines with 12 nozzles on each line. Water quenching flow is adjusted into a range of 10 to 60 m3 per hour, and the advance speed of the tube is controlled from 5 to 25 meters per minute. Additionally, following pinch rollers are set up to produce a rotation over the tube.

[0065] The ultra high strength steel tube so manufactured is passed through different finishing steps, straightened at known rotary straightening equipment, and non-destructively tested by one or more of the different known techniques. Preferably, for this kind of applications tubes should be tested by means of both known ultrasound and electromagnetic techniques.

[0066] The tubing after heat treatment can be chemically processed to obtain a tube with a desirable appearance and very low surface roughness. For example, the tube could be pickled in a sulfuric acid and hydrochloric acid solution, phosphated using zinc phosphate, and oiled using a petroleum-based oil, a water-based oil, or a mineral oil.

[0067] A steel tube obtained by the first or second described methods have the following minimum mechanical properties:

Yield Strength	about 110 ksi (758 MPa) minimum
Tensile Strength	about 145 ksi (1000 MPa) minimum
Elongation	about 9% minimum

[0068] The yield strength, tensile strength, and elongation are to be performed according to the procedures described in the Standards ASTM E8. For the tensile test, a full size specimen for evaluating the whole tubular section is preferred.

[0069] Flattening testing shall conform to the requirements of Specification DOT 39 of 49 CFR, Paragraph 178.65. Therefore, a tube section shall not crack when flattened with a 60 degree angled V-shaped tooling, until the opposite sides are 6 times the tube wall thickness apart. This test is fully met by the steel developed.

[0070] In order to obtain a good balance between strength and toughness, the prior (sometimes referred to as former) austenitic grain size shall be preferably 7 or finer, and more preferably 9 or finer, as measured according to ASTM E-112 Standard. This is accomplished thanks to the extremely short heating cycle during austenitizing.

[0071] The steel tube obtained by the described method shall have the stated properties in order to comply with the requirements stated for the invention.

[0072] The demand of the industry is continuously pushing roughness requirements to lower values. The present invention has a good visual appearance, with, for example, a surface finish of the finished tubing of 3.2 microns maximum, both at the external and internal surfaces. This requirement is obtained through cold drawing, short austenizing times, reducing or neutral atmosphere tempering, and an adequate surface chemical conditioning at different steps of the process.

[0073] A hydroburst pressure test shall be performed by sealing the ends of the tube section, for example, by welding flat steel plates to the ends of the tube. It is important that a 300 mm tube section remains constraint free so that full hoop stress can develop. The pressurization of the tube section shall be performed by pumping oil, water, alcohol or a mixture of them.

[0074] The burst test pressure requirement depends on the tube size. When burst tested, the ultra high strength steel seamless tube has a guaranteed ductile behavior at -60°C . Tests performed on the samples produced show that this grade has a guaranteed ductile behavior at -60°C ., with a ductile-to-brittle transition temperature below -60°C .

[0075] The inventors have found that a far more representative validation test is the burst test, performed both at ambient and at low temperature, instead of Charpy impact test (according to ASTM E23). This is due to the fact that relatively thin wall thicknesses and small outside diameter in these products are employed, therefore no standard ASTM specimen for Charpy impact test can be machined from the tube in the transverse direction. Moreover, in order to get this subsize Charpy impact probe, a flattening deformation has to be applied to a curved tube probe. This has a sensible effect on the steel mechanical properties, in particular the impact strength. Therefore, no representative impact test is obtained with this procedure.

Examples Using Alternative, Low Carbon, Low Alloy Steels

[0076] Applicants have discovered that a high speed quench without a temper is a critical aspect of the present invention. Steels which are lower alloy and less expensive than prior art chemistries when treated by a particular heating and high speed quench can meet or exceed the standards discussed hereinbefore.

[0077] The above defined, novel Steels A, B, C, D and E are alternative steels that were analyzed using the preferred method, wherein a very fast induction furnace austenizing with a high speed quench was used instead of adding a tempering step. Surprisingly, when control testing was done with certain of these novel steels wherein less than a high speed quench, i.e., a normal quenching process was employed or a tempering step, as described hereinbefore, was employed, the tests showed significantly poorer characteristics.

High Speed Quench and no Temper Process with Alternative Including Lower Cost Steels According to the Preferred Method

[0078] The parameters used for high speed quench tests on Steel E samples were as follows: Water flow of 40 m³/hr ; Speed advance tube of 20 m/min.; Inductor power of 80% Austenitizing temperature: 880-940°, aim 920°; Martensite transformation on OD surface and core material was observed.

[0079] FIG. 1 shows core material with 100% Martensite transformation for Steel E.

[0080] Steel E, which has chemistry similar to a low alloy SAE 1010 grade steel, did not achieved minimum expected values. when subjected to high speed quenching.

[0081] Test results were as follows:

Sample	YS (Mpa)	YS (Psi)	% Elo	UTS (Mpa)	UTS (Psi)
20476	561	81414	26	835	121140
20477	570	82680	32	827	119988
20478	538	78086	32	802	116446
20479	552	80177	32	831	120613

[0082] Likewise, burst tests at low temperature (-60°C .) were performed in order to observe the behavior and type of crack. FIG. II shows tested burst samples for Steel E. Both presented a ductile behavior.

[0083] A control test on Steel E involved a normal quenching process was performed, results as follows:

Sample	YS (Mpa)	YS (Psi)	% Elo	UTS (Mpa)	UTS (Psi)
20480	478	69367	28	721	104683
20481	469	68059	32	713	103531
20482	497	72226	32	714	103574
20483	478	69367	32	703	102009

[0084] FIG. III presents the core structures for Steel E using normal quenching process. Some ferrite structure is observed along the wall thickness.

[0085] Steel D was discovered to be very promising because of the high performance to cost value it presented. Steel D was selected to manufacture tubing according to the preferred method. Measured chemical composition of samples of Steel D that were used for high speed quench tests were as follows:

Element	% Value
C	0.11
Mn	1.07
S	0.002
P	0.008
Si	0.08
V	0.08
Al	0.03
Nb	0.008

[0086] The parameters used for the high speed quench tests on samples of Steel D were as follows:

Quenching process was conducted controlling austenite temperature into 920-940° C.

Water flow of 40 m³/hr

Speed advance tube of 10 m/min.

Inductor power of 62% total capacity (500 Kw)

A rotation over the tube was given with an angle of pinch rolls of 17°

[0087] Test results for high speed quenched on samples of Steel D, were as follows:

Sample	YS (Mpa)	YS (Psi)	% Elo	UTS (Mpa)	UTS (Psi)
19605	860	124810	20	1209	175388
19606	781	113360	19	1184	171860

[0088] FIG. IV shows that a high speed quench Steel D microstructure that presents Martensite at 100% and a completely quenched transformation.

[0089] Likewise, burst tests at low temperature (−60° C.) were performed in order to observe the behavior and type of crack. Figure V shows tested burst samples for Steel D. Both presented a ductile behavior.

[0090] A control test on Steel D involving a normal quenching process was performed, results as follows:

Sample	YS (Mpa)	YS (Psi)	% Elo	UTS (Mpa)	UTS (Psi)
19609	618	89635	24	861	124952
19610	586	85060	24	882	127967

[0091] FIG. VI presents the core structures for Steel D using normal quenching process.

[0092] Steel B was selected to manufacture tubing according to the preferred method. Measured chemical composition of samples of Steel B that were used for high speed quench tests were as follows:

Element	% Value
C	0.10
Mn	1.09
S	0.001
P	0.011
Si	0.28
V	0.038
Al	0.035
Cr	0.68
Mo	0.41
Nb	0.005

[0093] The parameters used for the high speed quench tests on samples of Steel B were as follows:

Quenching process was conducted controlling austenite temperature into 920-940° C. Water flow of 40 m3/hr

Speed advance tube of 10 m/min.

Inductor power of 70% total capacity (500 Kw)

A rotation over the tube was given with an angle of pinch rolls of 17°

[0094] Test results for high speed quenched on samples of Steel B, were as follows:

Sample	YS (Mpa)	YS (Psi)	% Elo	UTS (Mpa)	UTS (Psi)
25222	940	136	22	1217	176
25002	914	132	24	1206	175

[0095] Likewise, burst tests at low temperature (−60° C.) were performed on Steel B in order to observe the behavior and type of crack, both presented a ductile behavior.

[0096] Steel A was selected to manufacture tubing according to the preferred method. Measured chemical composition of samples of Steel A that were used for high speed quench tests were as follows:

Element	% Value
C	0.10
Mn	1.23
S	0.002
P	0.008
Si	0.27
V	0.002
Al	0.035
Cr	0.11
Mo	0.05
Ni	0.34

[0097] The parameters used for the high speed quench tests on samples of Steel A were as follows:

Quenching process was conducted controlling austenite temperature into 920-940° C.

Water flow of 50 m3/hr

Speed advance tube of 20 m/min.

Inductor power of 90% total capacity (500 Kw)

A rotation over the tube was given with an angle of pinch rolls of 17

[0098] Test results for high speed quenched on samples of Steel A, were as follows:

Sample	YS (Mpa)	YS (Psi)	% Elo	UTS (Mpa)	UTS (Psi)
20313	920	133	22	1230	178
21442	883	128	20	1195	173

[0099] Likewise, burst tests at low temperature (−60° C. and −100° C.) were performed on Steel A in order to observe the behavior and type of crack, both presented a ductile behavior.

Control Tests with a High Quench Followed by a Temper Process with Alternative Lower Cost Steels

[0100] Once samples of the preferred Steel D were found to yield surprising mechanical values upon using a high

speed quenching according to the preferred method, a tempering then was performed in order to determine the effect of adding a temper upon the mechanical properties.

[0101] A tempering heat treatment was conducted at 580° C. for total time of 15 minutes. The UTS average was 116 Ksi (805 MPa), which do not meet the expected values

[0102] While preferred embodiments of our invention have been shown and described in order to comply with the description and enablement requirements of 35 USC §112, it is to be understood that the scope of the invention is not limited to any embodiment that has been described, but solely is to be defined by the scope of the appended claims.

We claim:

1. A low carbon alloy steel tube consisting essentially of, by weight: about 0.06% to about 0.18% carbon; about 0.5% to about 1.5% manganese; about 0.1% to about 0.5% silicon; up to about 0.015% sulfur; up to about 0.025% phosphorous; up to about 0.50% nickel; about 0.1% to about 1.0% chromium; about 0.1% to about 1.0% molybdenum; about 0.01% to about 0.10% vanadium; about 0.01% to about 0.10% titanium; about 0.05% to about 0.35% copper; about 0.010% to about 0.050% aluminum; up to about 0.05% niobium; up to about 0.15% residual elements; and the balance iron and incidental impurities, wherein the steel tube has a tensile strength of at least about 145 ksi and has a ductile-to-brittle transition temperature below -60° C.

2. The low carbon alloy steel tube of claim 1, wherein the steel tube consists essentially of, by weight: about 0.07% to about 0.12% carbon; about 1.00% to about 1.40% manganese; about 0.15% to about 0.35% silicon; up to about 0.010% sulfur; up to about 0.015% phosphorous; up to about 0.20% nickel; about 0.55% to about 0.80% chromium; about 0.30% to about 0.50% molybdenum; about 0.01% to about 0.07% vanadium; about 0.01% to about 0.05% titanium; about 0.15% to about 0.30% copper; about 0.010% to about 0.050% aluminum; up to about 0.05% niobium; up to about 0.15% residual elements; and the balance iron and incidental impurities.

3. The low carbon alloy steel tube of claim 1, wherein the steel tube consists essentially of, by weight: about 0.08% to about 0.11% carbon; about 1.03% to about 1.18% manganese; about 0.15% to about 0.35% silicon; up to about 0.003% sulfur; up to about 0.012% phosphorous; up to about 0.10% nickel; about 0.63% to about 0.73% chromium; about 0.40% to about 0.45% molybdenum; about 0.03% to about 0.05% vanadium; about 0.025% to about 0.035% titanium; about 0.15% to about 0.30% copper; about 0.010% to about 0.050% aluminum; up to about 0.05% niobium; up to about 0.15% residual elements; and the balance iron and incidental impurities.

4. The low carbon alloy steel tube of claim 1, wherein the steel tube has a yield strength of at least about 125 ksi.

5. The low carbon alloy steel tube of claim 1, wherein the steel tube has a yield strength of at least about 135 ksi.

6. The low carbon alloy steel tube of claim 1, wherein the steel tube has an elongation at break of at least about 9%.

7. The low carbon alloy steel tube of claim 1, wherein the steel tube has a hardness of no more than about 40 HRC.

8. The low carbon alloy steel tube of claim 1, wherein the steel tube has a hardness of no more than about 37 HRC.

9. The low carbon alloy steel tube of claim 1, wherein the steel tube has a carbon equivalent of less than about 0.63%,

the carbon equivalent being determined according to the formula: $Ceq = \% C + \% Mn/6 + (\% Cr + \% Mo + \% V)/5 + (\% Ni + \% Cu)/15$.

10. The low carbon alloy steel tube of claim 9, wherein the steel tube has a carbon equivalent of less than about 0.60%.

11. The low carbon alloy steel tube of claim 9, wherein the steel tube has a carbon equivalent of less than about 0.56%.

12. The low carbon alloy steel tube of claim 1, wherein the steel tube has a maximum microinclusion content of 2 or less—thin series—, and level 1 or less—heavy series—, measured in accordance with ASTM E45 Standard-Worst Field Method (Method A).

13. The low carbon alloy steel tube of claim 1, wherein the steel tube has a maximum microinclusion content measured in accordance with ASTM E45 Standard-Worst Field Method (Method A), as follows:

Inclusion Type	Thin	Heavy
A	0.5	0
B	1.5	1.0
C	0	0
D	1.5	0.5

14. The low carbon alloy steel tube of claim 13, wherein oversize inclusion content with 30 μ m or less in size is obtained.

15. The low carbon alloy steel tube of claim 14, wherein the total oxygen content is limited to 20 ppm.

16. The low carbon alloy steel tube of claim 1, wherein the tube has a seamless configuration.

17. A stored gas inflator pressure vessel comprising the low carbon alloy steel tube of claim 1.

18. An automotive airbag inflator comprising the low carbon alloy steel tube of claim 1.

19. A low carbon alloy steel tube consisting essentially of, by weight: about 0.08% to about 0.11% carbon; about 1.03% to about 1.18% manganese; about 0.15% to about 0.35% silicon; up to about 0.003% sulfur; up to about 0.012% phosphorous; up to about 0.10% nickel; about 0.63% to about 0.73% chromium; about 0.40% to about 0.45% molybdenum; about 0.03% to about 0.05% vanadium; about 0.025% to about 0.035% titanium; about 0.15% to about 0.30% copper; about 0.010% to about 0.050% aluminum; up to about 0.05% niobium; up to about 0.15% residual elements; and the balance iron and incidental impurities, wherein the steel tube has a yield strength of at least about 135 ksi, a tensile strength of at least about 145 ksi, an elongation at break of at least about 9%, a hardness of no more than about 37 HRC, and has a ductile-to-brittle transition temperature below -60° C.

20. The low carbon alloy steel tube of claim 19, wherein the tube has a seamless configuration.

21. A stored gas inflator pressure vessel comprising the low carbon alloy steel tube of claim 19.

22. An automotive airbag inflator comprising the low carbon alloy steel tube of claim 19.

23. A method of manufacturing a length of steel tubing for a stored gas inflator pressure vessel, comprising the following steps: producing a length of tubing from a steel material consisting essentially of, by weight: about 0.06% to about 0.18% carbon, about 0.5% to about 1.5% manganese, about 0.1% to about 0.5% silicon, up to about 0.015% sulfur, up

to about 0.025% phosphorous, up to about 0.50% nickel, about 0.1% to about 1.0% chromium, about 0.1% to about 1.0% molybdenum, about 0.01% to about 0.10% vanadium, about 0.01% to about 0.10% titanium, about 0.05% to about 0.35% copper, about 0.010% to about 0.050% aluminum, up to about 0.05% niobium, up to about 0.15% residual elements, and the balance iron and incidental impurities; subjecting the steel tubing to a cold-drawing process to obtain desired dimensions; austenizing by heating the cold-drawn steel tubing in an induction-type austenizing furnace to a temperature of at least Ac3, at a heating rate of at least about 100° C. per second; after the heating step, quenching the steel tubing in a quenching fluid until the tubing reaches approximately ambient temperature, at a cooling rate of at least about 100° C. per second; and after the quenching step, tempering the steel tubing for about 2-30 minutes at a temperature below Ac1.

24. The method of claim 23, wherein the steel tubing produced consists essentially of, by weight: about 0.07% to about 0.12% carbon, about 1.00% to about 1.40% manganese, about 0.15% to about 0.35% silicon, up to about 0.010% sulfur, up to about 0.015% phosphorous, up to about 0.20% nickel, about 0.55% to about 0.80% chromium, about 0.30% to about 0.50% molybdenum, about 0.01% to about 0.07% vanadium, about 0.01% to about 0.05% titanium, about 0.15% to about 0.30% copper, about 0.010% to about 0.050% aluminum, up to about 0.05% niobium, up to about 0.15% residual elements, and the balance iron and incidental impurities.

25. The method of claim 23, wherein the steel tubing produced consists essentially of, by weight: about 0.08% to about 0.11% carbon, about 1.03% to about 1.18% manganese, about 0.15% to about 0.35% silicon, up to about 0.003% sulfur, up to about 0.012% phosphorous, up to about 0.10% nickel, about 0.63% to about 0.73% chromium, about 0.40% to about 0.45% molybdenum, about 0.03% to about 0.05% vanadium, about 0.025% to about 0.035% titanium, about 0.15% to about 0.30% copper, about 0.010% to about 0.050% aluminum, up to about 0.05% niobium, up to about 0.15% residual elements, and the balance iron and incidental impurities.

26. The method of claim 23, wherein the finished steel tubing has a yield strength of at least about 125 ksi.

27. The method of claim 23, wherein the finished steel tubing has a yield strength of at least about 135 ksi.

28. The method of claim 23, wherein the finished steel tubing has a tensile strength of at least about 145 ksi.

29. The method of claim 23, wherein the finished steel tubing has an elongation at break of at least about 9%.

30. The method of claim 23, wherein the finished steel tubing has a hardness of no more than about 40 HRC.

31. The method of claim 23, wherein the finished steel tubing has a hardness of no more than about 37 HRC.

32. The method of claim 23, wherein the finished steel tubing has a ductile-to-brittle transition temperature below -60° C.

33. The method of claim 23, wherein in the austenizing heating step, the steel tubing is heated to a temperature between about 920-1050° C.

34. The method of claim 33, wherein in the austenizing heating step, the steel tubing is heated at a rate of at least about 200° C. per second.

35. The method of claim 23, wherein in the quenching step, the steel tubing is cooled at a rate of at least about 200° C. per second.

36. The method of claim 23, wherein in the tempering step, the steel tubing is tempered at a temperature between about 400-600° C.

37. The method of claim 36, wherein in the tempering step, the steel tubing is tempered for about 4-20 minutes.

38. The method of claim 23, further comprising a finishing step wherein the tempered steel tubing is pickled, phosphated, and oiled.

39. A method of manufacturing a length of steel tubing for a stored gas inflator pressure vessel, comprising the following steps: producing a length of tubing from a steel material consisting essentially of, by weight: about 0.08% to about 0.11% carbon, about 1.03% to about 1.18% manganese, about 0.15% to about 0.35% silicon, up to about 0.003% sulfur, up to about 0.012% phosphorous, up to about 0.10% nickel, about 0.63% to about 0.73% chromium, about 0.40% to about 0.45% molybdenum, about 0.03% to about 0.05% vanadium, about 0.025% to about 0.035% titanium, about 0.15% to about 0.30% copper, about 0.010% to about 0.050% aluminum, up to about 0.05% niobium, up to about 0.15% residual elements, and the balance iron and incidental impurities; subjecting the steel tubing to a cold-drawing process to obtain desired dimensions; austenizing by heating the cold-drawn steel tubing in an induction-type austenizing furnace to a temperature between about 920-1050° C., at a heating rate of at least about 200° C. per second; after the heating step, quenching the steel tubing in a water-based quenching solution until the tubing reaches approximately ambient temperature, at a cooling rate of at least about 200° C. per second; and after the quenching step, tempering the steel tubing for about 4-20 minutes at a temperature between about 450-550° C., a finishing step wherein the tempered steel tubing is pickled, phosphated, and oiled, wherein the finished steel tubing has a yield strength of at least about 135 ksi, a tensile strength of at least about 145 ksi, an elongation at break of at least about 9%, a hardness of no more than about 37 HRC, a ductile-to-brittle transition temperature below -60° C. and a good surface appearance.

40. A method of manufacturing a length of steel tubing for a stored gas inflator pressure vessel, comprising the following steps: producing a length of tubing from a steel material consisting essentially of, by weight: about 0.06% to about 0.18% carbon, about 0.3% to about 1.5% manganese, about 0.05% to about 0.5% silicon, up to about 0.015% sulfur, up to about 0.025% phosphorous, and at least one of the following elements: up to about 0.30% vanadium, up to about 0.10% aluminum, up to about 0.06% niobium, up to about 1% chromium, up to about 0.70% nickel, up to about 0.70% molybdenum, up to about 0.35% copper, up to about 0.15% residual elements, and the balance iron and incidental impurities; subjecting the steel tubing to a cold-drawing process to obtain desired dimensions; austenizing by heating the cold-drawn steel tubing in an induction-type austenizing furnace to a temperature of at least Ac3, at a heating rate of at least about 100° C. per second; after the heating step, quenching the steel tubing in a quenching fluid until the tubing reaches approximately ambient temperature, at a cooling rate of at least about 100° C. per second, wherein the steel tube has a tensile strength of at least about 145 ksi and has a ductile-to-brittle transition temperature below -60° C.

41. The method of claim 40, wherein the steel tubing produced consists essentially of, by weight: about 0.07% to about 0.12% carbon, about 0.60% to about 1.40% manganese, about 0.05% to about 0.40% silicon, up to about 0.010% sulfur, up to about 0.02% phosphorous, and at least one of the following elements: up to about 0.20% vanadium, up to about 0.07% aluminum, up to about 0.04% niobium, up to about 0.8% chromium, up to about 0.50% nickel, up to about 0.50% molybdenum, up to about 0.35% copper, up to about 0.15% residual elements, and the balance iron and incidental impurities, wherein the steel tube has a tensile strength of at least about 160 ksi and has a ductile-to-brittle transition temperature below -60°C .

42. The method of claim 40, wherein the steel tube has a carbon equivalent of less than about 0.52%, the carbon equivalent being determined according to the formula: $\text{Ceq} = \% \text{C} + \% \text{Mn}/6 + (\% \text{Cr} + \% \text{Mo} + \% \text{V})/5 + (\% \text{Ni} + \% \text{Cu})/15$.

43. The method of claim 41, wherein the steel tube has a carbon equivalent of less than about 0.48%, the carbon equivalent being determined according to the formula: $\text{Ceq} = \% \text{C} + \% \text{Mn}/6 + (\% \text{Cr} + \% \text{Mo} + \% \text{V})/5 + (\% \text{Ni} + \% \text{Cu})/15$.

44. The method of claim 40, wherein the finished steel tubing has an elongation at break of at least about 9%.

45. The method of claim 40, wherein in the austenizing heating step, the steel tubing is heated to a temperature between about 860 - 1050°C .

46. The method of claim 40, wherein in the austenizing heating step, the steel tubing is heated at a rate of at least about 200°C . per second.

47. The method of claim 40, wherein in the quenching step, the steel tubing is cooled at a rate of at least about 200°C . per second.

48. A method of manufacturing a length of steel tubing for a stored gas inflator pressure vessel, comprising the following steps: producing a length of tubing from a steel material consisting essentially of, by weight: about 0.07% to about 0.12% carbon, about 0.60% to about 1.40% manganese, about 0.05% to about 0.40% silicon, up to about 0.010% sulfur, up to about 0.02% phosphorous, maximum 0.20% vanadium, up to about 0.07% aluminum, up to about 0.04% niobium, up to about 0.8% chromium, up to about 0.50% nickel, up to about 0.50% molybdenum, up to about 0.35% copper, up to about 0.15% residual elements, and the balance iron and incidental impurities; subjecting the steel tubing to a cold-drawing process to obtain desired dimensions; austenizing by heating the cold-drawn steel tubing in an induction-type austenizing furnace to a temperature between about 860 - 1050°C ., at a heating rate of at least about 200°C . per second; after the heating step, quenching the steel tubing in a water-based quenching solution at a cooling rate of at least about 200°C . per second; wherein the finished steel tubing has a tensile strength of at least about 160 ksi, an elongation at break of at least about 9%, and a ductile-to-brittle transition temperature below -60°C . and preferably below 100°C .

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