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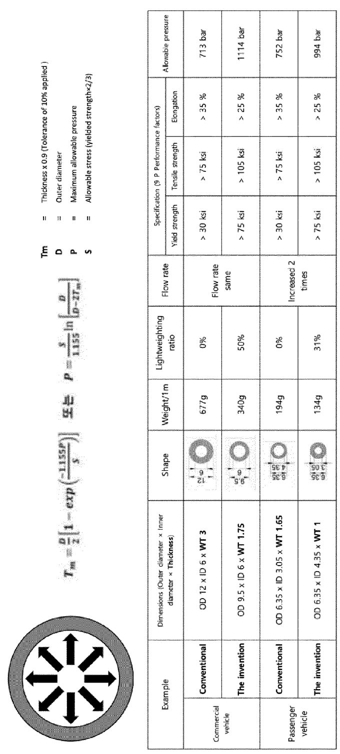
(54) **HIGH STRENGTH FUEL PIPING MATERIAL FOR HYDROGEN MOBILITY**

(57) An objective of the present disclosure is to provide a high strength and lightweight fuel pipe for a mobility by increasing a nickel equivalent, configuring an alloy composition having price competitiveness, and designing optimized pipe dimensions to a pipe for carrying hydrogen formed in the alloy composition under applicable pressure.

According to the objective, the present disclosure provides an alloy material having a Ni equivalent (Ni_{eq}) over 28.5% by controlling the composition of C, Si, Mn, P, S, Ni, Cr, and Mo, a pipe is machined using the alloy material, and a high-strength pipe of about 1/8 hard is provided by applying a strength increasing technology using work hardening and heat treatment.

FIG. 2



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Description

[Field of Invention]

[0001] The present disclosure relates to a hydrogen fuel tube (piping material) technology for a hydrogen mobility such as a hydrogen vehicle, the technology being able to prevent hydrogen embrittlement and reduce weight by increasing strength.

[Background Art]

[0002] A hydrogen vehicle that is an eco-friendly vehicle has been popularized. A hydrogen fuel cell system has a problem that when hydrogen is contained in the metal of a hydrogen fuel pipe, toughness decreases, so the pipe easily breaks. This phenomenon accelerates at a low temperature and is generated in a strain-induced martensite structure in the case of stainless steel. As a plan for solving this problem, it may be considered to suppress a bet structure that is strain-induced martensite of stainless steel by increasing the content of fcc stabilizing nickel.

[0003] Relevant technologies are as follows.

[0004] Korean Patent Application Publication No. 10-2022-0010184 is based on a composition that can improve hydrogen embrittlement resistance by having a nickel equivalent over 28.5% in austenite-based stainless steel 316, but is not satisfactory when taking aim at reducing the weight of austenite-based stainless steel.

[0005] Further, Japanese Re-publication Patent No. WO2015/098981 (2017.03.23.) increases hydrogen embrittlement resistance of a surface by forming a plurality of aluminum-based special coatings having a thickness of 3~35μm on a mother material, but does not increase hydrogen embrittlement resistance of alloy steel itself.

[0006] Further, Patent Application Publication No. 2011-026650 (2011.02.10.) is focused on increasing insufficient toughness and ductility at high strength under 1% (preferably, prescribed at 0.9%) by prescribing a nickel value under 12% (preferably, prescribed at 10.6%) as a steel wire that is used for high-strength shaft, pin, spring, rope, etc. having high hydrogen embrittlement resistance and by putting in a large amount of copper over an impurity level, and on minimizing strain-induced martensite by minimizing internal stress (0$\pm$400MPa). For reference, a strain-induced martensite structure that is generated in austenite-based stainless steel is removed when heat treatment over 400°C is performed.

[0007] As for Korean Patent Application Publication No. 10-2018-0111416 (2018.10.11.), a stainless pipe that is very soft and has ductility at the level of a copper pipe by inducing excessive grain growth through solid solution heat treatment for a long time, thereby replacing copper and reducing weight in comparison to copper. Further, this is an invention that reduces weight by decreasing thickness by simply changing the steel grade without considering problems of the corrosion resistance characteristic of copper or the possibility of pitting corrosion of stainless and work hardening, so it can be considered as an invention that is not actually applied.

[Disclosure]

[Technical Problem]

[0008] An objective of the present disclosure is to provide a high strength and lightweight fuel pipe for a mobility by increasing a nickel equivalent, configuring an alloy composition having price competitiveness, and designing optimized pipe dimensions to a pipe for carrying hydrogen formed in the alloy composition under applicable pressure.

[Technical Solution]

[0009] According to the objective, the present disclosure provides an alloy material having a Ni equivalent (Ni_{eq}) over 28.5 % by controlling the composition of C, Si, Mn, P, S, Ni, Cr, and Mo, a pipe is machined using the alloy material, and a high-strength pipe of about 1/8 hard is provided by applying a strength increasing technology using work hardening and heat treatment. It is included in an alloy corresponding to 316 and 316-class alloys. The structure of 1/8 hard in the above description means a recovery heat treatment structure after drawing.

[0010] The high-strength pipe can be thinned by applying a technology of increasing strength, the pipe can be designed to have a smaller thickness than the related art for an operating pressure reference by reversely calculating a pipe thickness from the allowable pressure and the allowable stress of a pipe for delivering hydrogen fuel of a hydrogen mobility such as a hydrogen vehicle, thereby providing a lightweighted and thinned pipe.

[0011] That is, the present disclosure provides

a hydrogen fuel pipe for a hydrogen mobility, wherein an alloy material having a Ni equivalent (Ni_{eq}) over 28.5% is configured by controlling the composition of C, Si, Mn, P, S, Ni, Cr, and Mo on the basis of 316-series stainless steel, and

a pipe is machined using the alloy material and has yield strength over 75 ksi, tensile strength over 105 ksi, and elongation over 18%.

[0012] The present disclosure provides a hydrogen fuel pipe for a hydrogen mobility,

wherein an alloy material having a Ni equivalent (Ni_{eq}) over 28.5% is configured by controlling the composition of C, Si, Mn, P, S, Ni, Cr, and Mo on the basis of 316-series stainless steel, and
yield strength is 55 ksi to less than, tensile strength is over 100 ksi, and elongation is over 25%.

[0013] In the above description, the thickness pipe is calculated by the following equation, and

allowable pressure is calculated over 500bar.

$$T_m = \frac{D}{2}\left[1 - \exp\left(\frac{-1.155P}{S}\right)\right] \; or \; P = \frac{S}{1.155}\ln\left[\frac{D}{D - 2T_m}\right]$$

where

$$Tm = \text{thickness x 0.9 (tolerance of 10\% applied)}$$

D = outer diameter, P = maximum allowable pressure

$$S = \text{allowable stress (yielded strength} \times (2/3))$$

[0014] In the above description,

a ratio of channel area/pipe area is calculated by the following equation,

$$\text{channel area(inner area)/pipe area(outer area)} = \pi\{(D-2 \text{ x } Tm)/2\}^2/\pi(D/2)^2$$

$$= (D - 2 \text{ x } Tm)^2/D^2$$

$$= \exp^2(-1.155P/S),$$

when design pressure or use pressure required by equipment or a facility at which the pipe is installed is 500~900bar, a ratio of channel area(inner area)/pipe area(outer area) of the pipe is over 35%, and
when design pressure or use pressure is 900~1200bar, the ratio of channel area(inner area)/pipe area(outer area) of the pipe is over 25%.

[0015] In the above description, a pipe using the alloy material undergoes work hardening that includes pilger rolling and drawing processes and increases strength of a pipe, and then undergoes heat treatment.
[0016] In the above description, the pipe is a metal structure pipe composed of a recovery structure.
[0017] A member for a hydrogen mobility to which the hydrogen fuel pipe for a hydrogen mobility is applied is provided.
[0018] In short, the present disclosure provides a hydrogen fuel pipe for a hydrogen mobility, wherein

① a Ni equivalent (Ni_{eq}) is set over 28.5% by controlling the composition of C, Si, Mn, P, S, Ni, Cr, and Mo on the basis of 316-series stainless steel,

② a work hardening process and heat treatment is performed,

③ a recovery structure is configured, and

④ specific yield strength, tensile strength, and elongation are satisfied.

[Advantageous Effects]

[0019] According to the present disclosure, a pipe for a hydrogen commercial vehicle that is manufactured by providing an alloy material having a Ni equivalent (Ni_{eq}) over 28.5 wt% and applying a technology of increasing strength through work hardening and heat treatment on the alloy material has a high-strength characteristic, so even though the inner diameters are the same and lightweighting of 50% is achieved, allowable pressure increases to 1114bar that is remarkably higher than 713bar of existing piping materials. Accordingly, it is possible to provide a pipe having a thickness that is smaller about a half than existing pipe thicknesses, whereby it is possible to achieve lightweighting over almost 50% in comparison to existing pipes.

[0020] Further, when the outer diameter of a pipe is maintained also for a pipe for a hydrogen passenger, the weight of the piping material can be reduced about 31%, and it is also possible to provide a pipe thinner than existing pipes, so the inner diameter increases and the flow rate of hydrogen can be increased. Allowable pressure also increases to 994bar higher than 752bar in the related art, so when the allowable pressure is adjusted to 700bar, lightweighting over 31% can be achieved.

[0021] That is, according to the present disclosure, since it is possible to increase the strength and reduce the weight of a pipe for a hydrogen vehicle, it is possible to improve the fuel efficiency of a hydrogen vehicle and reduce the volume.

[0022] Further, the allow of the present disclosure has a high nickel equivalent, but the composition of Mn and Cr of the composition of the alloy material is increased higher than existing alloy materials, so the alloy material can have price competitiveness and the weight thereof is reduced, whereby the price per weight is further decreased and the price competitiveness is further increased.

[Description of Drawings]

[0023]

FIG. 1 is a table comparing the composition of an alloy material of the present disclosure with an existing one;

FIG. 2 is a table for describing a pipe that can be thinned and reduced in weight when an alloy material according to the present disclosure is applied;

FIG. 3 is a picture exemplifying downsizing and lightweighting of a manifold as a part to which a piping material of the present disclosure can be applied;

FIG. 4 is a table for describing price competitiveness of a piping material of the present disclosure;

FIG. 5 is a table showing calculation of the ratio of a channel cross-sectional area (inner cross-sectional area)/channel-included pipe cross-sectional area (outer cross-sectional area) for a piping material of the present disclosure;

FIG. 6 is a conceptual diagram of a pilger rolling process;

FIG. 7 is a conceptual diagram of a drawing process of a pipe;

FIG. 8 shows a microstructure (plastic working-deformed structure) when there is no heat treatment after plastic working;

FIG. 9 shows a microstructure (recovery structure similar to a deformed structure) when recovery heat treatment is applied after plastic working; and

FIG. 10 shows a microstructure (recrystalized structure) when annealing heat treatment is performed after plastic working.

[Mode for Invention]

[0024] Hereinafter, preferred embodiments of the present disclosure will be described in detail with reference to the accompanying drawings.

[0025] In order to manufacture a hydrogen fuel tube piping material, which can prevent hydrogen embrittlement and reduce weight by increasing strength, for a hydrogen mobility such as a hydrogen vehicle, fcc structure stability is increased by increasing a Ni eq. (nickel equivalent, wt%) in a stainless steel alloy, thereby suppressing strain-induced martensite bet of stainless steel.

[0026] A nickel equivalent of an alloy material containing C, Si, Mn, Ni, Cr, and Mo is obtained as follows.

$$\text{Ni eq. (nickel equivalent, wt\%)} = 12.6\times C + 0.35\times Si + 1.05\times Mn + Ni + 0.65\times Cr + 0.98\times Mo$$

[0027] A nickel equivalent means the ratio of an element acting like nickel in an alloy (an alloy technology of a Ni eq. over 28.5% in an alloy within a 316L class has been know in relation to container boss part application 316L of compressed hydrogen gas high court KGS AC118. A nickel equivalent that is required for an alloy when high-pressure hydrogen gas is used at -10 - -40 °C. Products called KGS AC118 correspond to this case.

[0028] When a hydrogen vehicle is driven in cold areas such as Finland and Sweden, the hydrogen vehicle is placed in a low-temperature environment like those areas, so a piping material for a hydrogen vehicle that satisfies the nickel equivalent over 28.5% is necessary.

[0029] The present disclosure designs a piping material for a hydrogen vehicle that has a high nickel equivalent exceeding 28.5% for stainless steel and increases allowable pressure of a pipe by performing work hardening and heat treatment to provide a high-strength property to the piping material, thereby achieving both lightweighting and price competitiveness by decreasing the thickness of the pipe.

[0030] FIG. 1 is a table comparing the composition of an alloy material of the present disclosure with an existing one.

[0031] According to the standards proposed by ASTM, a nickel equivalent of 316L is 22.36-+31.5% and a corresponding composition of C, Si, Mn, P, S, Ni, Cr, and Mo has been exemplified. Minimum values and maximum values are proposed for the components Ni, Cr, and Mo. Further, the current nickel equivalent of domestic mother pipes is 25.99% and a corresponding alloy composition has also been proposed.

[0032] The present disclosure has to control a nickel equivalent of a piping material over 28.5%. FIG. 1 shows an example.

[0033] That is, there is provided an alloy material containing C of 0.005-0.015, Si of 0.35-0.45, Mn of 1.55-1.65, P of 0.027-0.035, S of 0.0075-0.0085, Ni of 13.15-13.25, Cr of 17.45-17.55, Mo of 2.55-2.65 wt%, and the balance of Fe, etc.

[0034] In this case, preferably, a piping material for a hydrogen vehicle in which a Ni equivalent (Ni_{eq}) is 29.07 wt% is provided by containing C of 0.010, Si of 0.40, Mn of 1.6, P는 0.03, S of 0.008, Ni of 13.2, Cr of 17.5, Mo of 2.6 wt%.

[0035] When using Ni and Mo, which are relatively expensive, less within a composition range within a standard, it is possible to manufacture an economically cheap alloy.

[0036] Such a high-nickel equivalent piping material is machined into a pipe shape through pilger rolling and drawing in the process in which it is manufactured into a pipe, and the pilger rolling and drawing themselves act as work hardening processes that increase the strength of the pipe. Further, strength is increased and resistance against hydrogen embrittlement is increased through heat treatment.

[0037] A pipe that has a high nickel equivalent and has undergone work hardening and heat treatment has high strength, so it can be thinned. That is, the maximum allowable pressure for a pipe for delivering hydrogen fuel of a hydrogen vehicle is increased due to high strength, the thickness of the pipe can be correspondingly decreased. This results in reduction of weight and material costs.

[0038] FIG. 2 shows thinning and lightweighting of a pipe that can be achieved when an alloy material according to the present disclosure is applied.

[0039] Calculation of the thickness and the allowable pressure of a pipe is based on the maximum allowable pressure calculation equation by American Society of Mechanical Engineers (ASME), which is as follows.

$$T_m = \frac{D}{2}\left[1 - \exp\left(\frac{-1.155P}{S}\right)\right] \; or \; P = \frac{S}{1.155}\ln\left[\frac{D}{D - 2T_m}\right]$$

where,

$$Tm = \text{thickness x } 0.9 \text{ (tolerance of 10\% applied)}$$

D = outer diameter, P = maximum allowable pressure

$$S = \text{allowable stress (yielded strength} \times (2/3))$$

[0040] It is possible to design a pipe thickness smaller than the existing one for an operating pressure reference by reversely calculating a pipe thickness from the allowable pressure and the allowable stress of a pipe, so it is possible to provide a weight-reduced and thinned pipe.

[0041] The piping material of the present disclosure has yield strength and tensile strength over 75ksi and over 105ksi, respectively, so they are considerably increased in comparison to existing products and the elongation is over 25%.

[Table 1]

Example of lightweighting and flow rate increase by thickness calculation predetermined use pressure							
	Dimensions (outer diamter × innner diameter × thickness)	Weight	lightweighting ratio	Specifications (9 p perfomance factors)			Allowable pressure
				Yield strength (ksi)	Tensile strength (ksi)	Elongation	ASME B31.3 Process Piping, Chapter IX High Pressure Piping.
for commercial vehicle (current)	OD 12 × ID 608 × WT 2.96	671g	0	> 30 ksi	> 75ksi	> 35%	700bar
for commercial vehicle (developed)	OD 7.92 × ID 608 × WT 0.92	161g	76% (inner diameter same)	> 75 ksi	> 105 ksi	> 25%	700bar
for passenger vehicle (current)	OD 6.35 × ID 3.21 × WT 1.57	188g	0	> 30 ksi	> 75 kis	> 35%	700bar
for passenger vehicle (developed)	OD 6.35 × ID 5.01 × WT 0.67	95g	49% (flow rate increased 2.4 times)	> 75 ksi	> 105 ksi	> 25%	700bar

[0042] According to the calculation values of the commercial vehicle pipes having the same inner diameter, the lightweighting ratio is 76%.

[0043] However, according to the calculation values of the passenger vehicles having the same outer diameter, the lightweighting ratio is 49% and the flow rate increases 2.4 times.

[0044] The pipe thickness calculated using an operating pressure of 700bar for the piping material according to the present disclosure is 1.75mm for passenger vehicles, as in FIG. 2, which is considerably smaller than 3mm in the related art, and the weight per 1m is 340g whereas it is 677g in the related art, so the weight is reduced almost about 50%. In the above case, the thickness may include an allowable tolerance of ±10%.

[0045] Further, as for passenger vehicles, the thickness is 1.65mm in the related art, but, in the present disclosure, the thickness of the piping material is 1.0mm and the weight per 1m is 134g whereas it is 194g in the related art, so the weight is reduced almost about 31%. In the above case, the thickness may include an allowable tolerance of ±10%.

[0046] Further, the allowable pressure according to the thickness of the piping material of the present disclosure increases from 713bar to 1114bar for commercial vehicles and from 752bar to 994bar for passenger vehicles. Accordingly, the flow rate can be increased about two times in comparison to the related art.

[0047] Therefore, there is a margin for allowable pressure in this embodiment, so it is possible to additionally reduce the weight.

[0048] Such thinning and lightweighting provides price competitiveness of a pipe and make it possible to decrease the weight and size of subsidiary materials for the pipe.

[0049] FIG. 3 is a picture exemplifying downsizing and lightweighting of a manifold as a part to which a piping material of the present disclosure can be applied.

[0050] FIG. 4 is a table for describing price competitiveness of a piping material of the present disclosure.

[0051] A lightweight pipe made of the pipe material according to the present disclosure has a reference unit cost of 71,420 Won per 6m under the assumption that it is sold in the unit of weight, which is about 30% cheaper than 101,534 Won. Drawing is added once in the process condition, unlike the related art, so the strength is further increased and the high-strength characteristic can be maintained in a heat treatment process. Accordingly, the manufacturing process cost increases, but the weight of the product decreases, so the price per unit length decreases.

[0052] FIG. 5 is a table showing calculation of the ratio of a channel cross-sectional area (inner cross-sectional area)/channel-included pipe cross-sectional area (outer cross-sectional area) for a piping material of the present disclosure.

[0053] When the yield strength that is a mechanical property of a pipe is over 55ksi or the tensile strength is over 100ksi, it is possible to provide a pipe of which the thickness is reduced with the same outer diameter in which the ratio of inner cross-sectional area/outer cross-sectional area of the pipe is over 35% when design pressure or use pressure required by equipment or a facility at which the pipe is installed by the maximum allowable pressure calculation equation by ASME is 500~900bar (e.g., 700bar) and in which the ratio of inner cross-sectional area/outer cross-sectional area of the pipe is over 25% when design pressure or use pressure is 900~1200bar (e.g., 1050bar).

[0054] That is, the hydrogen fuel pipe for a hydrogen mobility provided by the present disclosure is made of an alloy material that is based on 316-series stainless steel and has a Ni equivalent (Ni_{eq}) 28.5% or more by controlling the composition of C, Si, Mn, P, S, Ni, Cr, and Mo and is machined into a pipe using the alloy material, thereby having properties of yield strength 75 ksi or more, tensile strength 105 ksi or more, and elongation 18% or more.

[0055] Further, the hydrogen fuel pipe for a hydrogen mobility is made of an alloy material that is based on 316-series stainless steel and has a Ni equivalent (Ni_{eq}) 28.5% or more by controlling the composition of C, Si, Mn, P, S, Ni, Cr, and Mo and is machined into a pipe using the alloy material, thereby having properties of yield strength of 55 ksi to less than 75 ksi, tensile strength 100 ksi or more, and elongation 25% or more.

[0056] The machining process includes recovery heat treatment that is a step before drawing for increasing the strength and recrystalization are generated, thereby making the piping material forms a recovery structure. The term "recovery structure" is a metal engineering terminology for metal structures and is generally used among those skilled in the art.

[0057] The alloy of the present disclosure is formed to suppress production of strain-induced martensite that is generated in plastic working to improve hydrogen embrittlement resistance. Unlike carbon steel or ferrite-based stainless steel that have a body centered cubic (BBC) structure, austenite-based stainless steel having a face centered cubic (FCC) structure has resistance against hydrogen embrittlement, and particularly, the 316L steel grade has high austenite stability, so it has been known as a steel grade having high hydrogen embrittlement resistance.

[0058] However, a body centered tetragonal (BCT) structure similar to the BCC structure that is generated due to high energy (stress) that is generated in plastic working is vulnerable to hydrogen, the same as the BCC structure, that is, acts as hydrogen embrittlement, so generation thereof should be minimized.

[0059] In order to minimize strain-induced martensite in the 316L steel grade, it can be seen from various scientific journals and research data that nickel should be contained over 12% (Thorsten Michler, Joerg Naumann, Martin Hock, Karl Berreth, Michael P. Balogh, Erich Sattler, "Microstructural properties controlling hydrogen environment embrittlement of cold worked 316 type austenitic stainless steels", Materials Science & Engineering A 628 (2015) 252-261).

[0060] Further, hydrogen embrittlement complexly acts also with low-temperature embrittlement and austenite-based materials have known as materials that do not have low-temperature embrittlement, but low-temperature hydrogen embrittlement is generated by due complex action at a low temperature under a hydrogen atmosphere.

[0061] In order to prevent this problem, the present disclosure increases a nickel equivalent that means stabilization contribution of an element that stabilizes austenite (FCC structure), thereby stabilizing hydrogen embrittlement at a low temperature.

[0062] It has been known that when a nickel equivalent is over 28.5%, it can be used even in the low temperature range of -40°C (T. Yamada and H. Kobayashi, "Criteria for Selecting Materials to be Used for Hydrogen Station Equipment," J. High Press. Gas Saf. Inst. Japan, vol. 49, pp. 885-893, 2013.)

[0063] (S. Matsuoka, J. Yamabe, and H. Matsunaga, "Criteria for determining hydrogen compatibility and the mechanisms for hydrogen-assisted, surface crack growth in austenitic stainless steels," Eng. Fract. Mech., vol. 153, pp. 103-127, 2016.)

[0064] In the case of a hydrogen vehicle and a charging station, there are portions at which temperature drops even to -40°C in the change process of high pressure ↔ low pressure, the nickel equivalent should be over 28.5%, and as described above, a 316L steel grade for a hydrogen pipe having a nickel value over 12% is applied.

[0065] Further, according to ASTM A269 standards, the nickel range of 316L is 10-15%. The alloy of the present disclosure is an alloy corresponding to stainless steel 316.

[0066] Processes of work hardening and heat treatment for a hydrogen pipe are as follows.

[0067] In the case of a seamless pipe, a pipe formed through refining-casting-extruding is decreased in cross-sectional area by cold working by pilger rolling and drawing and is formed in desired dimensions, whereby a piping material having precise dimensions is manufactured.

[0068] A pilger rolling process and cold working are processes of forming a metal tube or a pipe by applying a plastic working method (see FIG. 6). A pilger rolling facility includes two circular dies having a U-shaped groove of which the shape gradually changes along a cylinder axis. The circular dies come in contact with a large pipe. The entire pipe is pressed by rolling the dies forward and backward, thereby reducing the diameter of the pipe to a desired level.

[0069] Drawing and heat treatment are repeatedly applied using the pipe, which has undergone recrystalization heat treatment after pilger rolling, as a mother material, thereby manufacturing a pipe having desired dimensions. Drawing is one of plastic working that manufacture a thin pipe by reducing the cross-sectional area by pulling and passing a tube material (pipes) through a die (see FIG. 7).

[0070] In the case of austenite-based steel grades, work hardening is generated due to movement and tangle of dislocations in a metal material by cord working, and when nickel and a nickel equivalent is not sufficiently high like the alloy stated in the present disclosure, an austenite structure is not stabilized, so a strain-induced martensite structure is generated in plastic working.

[0071] The reason that austenite-based stainless that is fundamentally not attracted to a magnet is slightly attracted to a magnet when plastic working is performed is generation of strain-induced martensite. Since strain-induced martensite also has the same magnetism as ferrite, so it can be measured through a ferrite meter.

[0072] In a common 304L steel grade, ferrite around 10% is measured in maximum machining. Ferrite around 3% is measured in a 316 steel grade having nickel of 10%.

[0073] Magnetism is not measured in the alloy in the present disclosure even though plastic working has been applied (very small amount cannot be measured).

[0074] In the present disclosure, the strengthening characteristic of work hardening is maintained through heat treatment within a temperature range that maintains dislocation tangle of plastic working, removes strain-induced martensite that may be generated in a very small amount, and secure elongation by removing stress for post-processing.

[0075] For heat treatment during a middle machining process before the final dimensions are obtained, solid solution heat treatment is performed so that next plastic working can be performed in a completely annealed state, and recovery treatment is performed after plastic working for the product (invention) with desired dimensions.

[0076] A heat treatment process of metal is composed of recovery, recrystalization, and grain growth.

[0077] A temperature range with poor recrystalization in 316 is 850-900°C. At temperatures over the range, recrystalization is generated and grain growth is generated. The present disclosure is characterized by performing recovery heat treatment preferably between 850-900°C about 5 minutes for a 316L steel grade.

[0078] A recovery heat treatment structure is as follows.

[0079] A recovery heat-treated structure (see FIG. 9) is not recrystalized (see FIG. 10, so a plastic-worked grain shape (see FIG. 8) is intactly shown and a structure (see FIGS. 8 and 9) in which line shapes due to unidirectional slip of dislocations are shown in the grains is maintained.

[0080] A high-strength piping material is characterized in that a shape maintaining dislocation slip without recrystalization serves to maintain high strength.

[0081] Specific yield strength, tensile strength, and elongation are as follows.

[0082] It is characterized by manufacturing a 316L pipe for high-strength hydrogen of YS 55KSI, TS 100KSI, and E25%↑ to YS 75KSI, TS 105KSI, and E25%↑ by performing recovery heat treatment within a range in which recrystalization is not generated at a temperature at which plasticity-induced martensite is little produced even in the plastic working and induced martensite that may be generated is sufficiently removed.

[0083] In general, a 316L steel grade that has undergone complete solid solution heat treatment has strength of YS 25KSI, TS 70KSI, and E35% or more. A product of the present disclosure is characterized by having twice to triple yield strength in comparison to that described above and having sufficient elongation for post-processing (forming, bending, etc.).

[0084] A pressure resistance characteristic of a piping material is based on a calculation equation based on a limit at which deformation does not occur, so allowable pressure increases in proportion to yield strength at which deformation starts to occur. A thicker material should be used as use pressure increases in a high-pressure pipe, but when the high-strength pipe for hydrogen by plastic working and recovery heat treatment proposed in the present disclosure is used, weight can be reduced by about 1/2 ~ 1/3. If a material has yield strength and tensile strength of YS 75KSI and TS 105KSI in the state in which recovery heat treatment has not been performed, the elongation is around 15%, which is not suitable for post-processing (bending and forming). It may be described that since recovery heat treatment is performed, slip shapes of dislocations remain, but stress is removed, so the limit for more deformation may increase. This is set as a design value of a company that requires a pipe for hydrogen.

[0085] Next, a detailed embodiment of manufacturing a high strength piping material for a hydrogen mobility is described. Described dimensions may be changed and a tolerance about ±5% may be allowed to the described dimensions.

Embodiment)

[0086] An extruded mother material of Φ65×6.5T is prepared and pilger rolling is performed on the extruding material, whereby a pipe of Φ38.1×3.0T is obtained. Accordingly, the cross-sectional reduction ratio becomes 72.3%.

[0087] Recrystalization heat treatment is performed on the obtained pipe, and annealing and solid solution heat treatment is performed at 1000 to 1200°C for 3 to 7 minutes, preferably, at 1080°C for 5 minutes.

[0088] Next, primary cold drawing is performed, whereby Φ31.8x2.4T is obtained. Accordingly, the cross-sectional reduction ratio becomes 33%.

[0089] Next, recrystalization heat treatment is performed. That is, annealing and solid solution heat treatment is performed at 1000 to 1200°C for 3 to 7 minutes, preferably, at 1080°C for 5 minutes.

[0090] Next, secondary cold drawing is performed, whereby Φ25.4x2.0T is obtained. Accordingly, the cross-sectional reduction ratio becomes 33.7%.

[0091] Next, recrystalization heat treatment is performed. That is, annealing and solid solution heat treatment is performed at 1000 to 1200°C for 3 to 7 minutes, preferably, at 1080°C for 5 minutes.

[0092] Next, third cold drawing is performed, whereby Φ19.05x1.65T is obtained. Accordingly, the cross-sectional reduction ratio becomes 38.7%.

[0093] Next, recovery heat treatment is performed. It is performed at 850 to 950°C for 3 to 7 minutes, preferably, at 900°C for 5 minutes, thereby recovering and removing magnetism (induced martensite).

Specific yield strength, tensile strength, and elongation are as follows.

[0094] It is characterized by manufacturing a 316L pipe for high-strength hydrogen of YS 55KSI, TS 100KSI, and E25%↑ to YS 75KSI, TS 105KSI, and E25%↑ by performing recovery heat treatment within a range in which recrystalization is not generated at a temperature at which induced martensite is little produced even in the plastic working and induced martensite that may be generated is sufficiently removed.

[0095] In general, a 316L steel grade that has undergone complete solid solution heat treatment has strength of YS 25KSI, TS 70KSI, and E35%T. The invention is characterized by having twice to triple yield strength in comparison to that described above and having sufficient elongation for post-processing (forming, bending, etc.).

Tension test			
Order	Yield strength	Tensile strength	Elongation
①Recovery heat treatment	90.65 KSI	110.42 KSI	23.55%
②Annealing heat treatment	38.38 KSI	81.49 KSI	51.46%
(3)No heat treatment	120.08 KSI	133.45 KSI	14.33%

Vickers Hardness Test(HV)				
Order	n1	n2	n3	Average
①Recovery heat treatment	227.0	237.3	236.1	233.47
② Annealing heat treatment	146.9	150.2	145.6	147.57

(continued)

Vickers Hardness Test(HV)				
Order	n1	n2	n3	Average
③No heat treatment	312.5	334.4	310.9	319.27

[0096] A pressure resistance characteristic of a piping material is based on a calculation equation based on a limit at which deformation does not occur, so allowable pressure increases in proportion to yield strength at which deformation starts to occur.
[0097] A thicker material should be used as use pressure increases in a high-pressure pipe, but when the high-strength pipe for hydrogen by plastic working and recovery heat treatment proposed in the present disclosure is used, 1/2 ~ 1/3 of pipe weight due to an existing pipe thickness can be reduced.
[0098] If a material has yield strength and tensile strength of YS 75KSI and TS 105KSI in the state in which recovery heat treatment has not been performed, the elongation is around 15% and the material is not suitable for post-processing (bending and forming).
[0099] It may be described that since recovery heat treatment is performed, slip shapes of dislocations remain, but stress is removed, so the limit for more deformation may increase, and it is set as a design value of a company that requires a pipe for hydrogen.
[0100] An entire processing method for manufacturing a pipe is as follows.

<Manufacturing of Alloy>

[0101] Since authentication and verification should be performed on a new developed steel grad, the product of the present disclosure is characterized by being able to be immediately applied by manufacturing it by adjusting chemical components within the range of the 316L steel grade which has been verified in dimensions.

Adjustment of Alloy Components

[0102] -C[Carbon] ~ 0.035%
[0103] Carbon fundamentally serves to improve strength and is an austenite stabilizing elements, but when a large amount of carbon is contained, it combines with chromium (Cr) of stainless, thereby producing a chromium carbide ($Cr_{23}C_6$) at a grain boundary, which reduces corrosion resistance. Since when the carbon content is high in the present disclosure that performs strengthening due to dislocation slip and tangle of plastic working, variables increase and integrity decreases, it is the most preferable to minimize the content of carbon, but decarbonization during refining and refining costs are increased, so preferably about 0.01% is taken as an aim in common VOD refining process.

-Si (Silicon) -1.00%

[0104] Silicon is a ferrite-based stabilizing element, produces an oxide after being put in as a deoxidizer in a refining process, becomes a slag rising up to the surface by high-temperature floatation and is then removed. Accordingly, when a large amount of silicon remains, it is handled as an impurity. When a large amount of silicon is contained, a large amount of nonmetallic inclusion is contained in a metal structure, thereby causing generation of cracks and deterioration of mechanical characteristics. Accordingly, it is the most preferable to minimize the content of silicon. However, about 0.4% is taken as an aim in common VOD refining process.

-Mn (Manganese) - 2.00%

[0105] Manganese is austenite-based stabilizing metal at a similar level to nickel and serves to produce MnS, prevent high-temperature cracks, and increase toughness by stably combining with S (sulfur), so it is preferable to put in manganese as much as possible. However, preferably, about 1.6% is taken as an aim for a stable value not exceeding a maximum limit within a range satisfying a 316L standard.

-P(Phosphorous) - 0.045%, S(Sulfur) - 0.030%

[0106] Phosphorous and sulfur are handled as representative impurities and have a possibility of generating intergranular cracks b producing an intermetallic compound with iron, so it is preferable to minimize them in a pipe for a hydrogen atmosphere, however, preferably, phosphorous of about 0.03% and sulfur of about 0.008% are taken as aims in a common VOD refining process.

-Ni(Nickel) 10.00%-14.00%

[0107] Nickel is a representative austenite stabilizing element, and when nickel is contained over 10% in the 316L steel grade, it forms an austenite phase of a stable FCC structure in hydrogen and serves to improve machinability and impact toughness, particularly, a low-temperature characteristic. It has been known that strain-induced martensite is little produced in an 316L steel grade containing nickel over 12%, so nickel greatly increases hydrogen embrittlement resistance, so it is preferable to put in nickel as much as possible, but it is expensive as rare metal, so, in accordance with the research results described above, preferably, about 13.2% is taken as an aim.

-Cr(Chromium) 16.00-18.00%

[0108] Chromium is a ferrite stabilizing element, is an important element that gives a stainless characteristic by producing a chromium oxide when it is contained over 12%, and serves to improve hardness and corrosion resistance. When the content of an austenite stabilizing element increases, a more stable alloy is formed without unbalance only when a ferrite stabilizing element is also slightly increased. Since chromium is put in as much as possible by a stabilized austenite elements, preferably, about 17.5% is taken as an aim.

Mo(Molybdenum) 2.0-3.0%

[0109] Molybdenum is a ferrite stabilizing element and produces an oxide on a chromium oxide passive coating layer when it is added, thereby greatly improve resistance particularly against pitting corrosion due to chlorine. Similar to chromium, a stabilized alloy is formed only when a ferrite stabilizing alloy is sufficiently put in an alloy containing a large amount of austenite stabilizing element, so preferably, about 2.6% is taken as an aim.

<Plastic Working>

[0110] The present disclosure manufactures a piping material for hydrogen that has precise dimensions and a lustrous surface by performing a pilger rolling process one time and repeatedly performing bright annealing and cold drawing processes on a seamless tube manufactured in accordance with the alloy manufacturing method described above.

<Description of Processes>

-Pilger rolling

[0111] A pilger rolling process acts in accordance with a malleability characteristic of metal, so the process is possible by setting a cross-section reduction ratio maximally at 80% with respect to stainless. Pilger has the advantage that it is possible to make a thickness value different to satisfy a process schedule determined in accordance with the dimensions of a final product.

-Recrystalization heat treatment

[0112] A material machined by pilger rolling and cold drawing undergoes plastic working by deformation, so heat treatment for recrystalization and solution is performed at a high temperature over 1040°C. In the case of the subject company, heat treatment is performed at a setting temperature of 1080°C for about 5 minutes in a continuous heat treatment furnace under a hydrogen atmosphere (99.999%).

[0113] In this case, three-step annealing heat treatment of recovery, recrystalization, and growth, and solid solution heat treatment are performed.

[0114] A washing process using and an organic solvent that removes a plastic working lubricant and contamination is performed first before bright annealing, and then a straightening correction process for the next process is performed on an intermediate product that is thermally deformed after bright annealing.

-Cold drawing

[0115] Cold drawing is a process that acts in accordance with the characteristic of toughness (longitudinal direction) unlike the malleability characteristic of a pilger rolling process, and generally, the toughness characteristic gives low machinability to a metal structure in comparison to the malleability characteristic, so cross-section reduction of maximally about 40% is possible. However, since a cold drawing process uses a mold having precise dimensions, it has the advantage that it is possible to more easily follow desired dimension tolerance and the production speed is high over 5 times the pilger rolling process.

[0116] Accordingly, a know-how of making start dimensions by performing once a pilger rolling process that can adjust a desired thickness using a malleability characteristic, and then making a precise piping material by performing a cold drawing process several times.

[0117] Bright annealing heat treatment, straightening correction, and bending (swaging) are performed before cold drawing, and bending cutting and washing using an organic solvent are performed after cold drawing.

-Final recovery heat treatment

[0118] Recovery heat treatment may be referred to as stress-relieved annealed, and according to heat treatment acting principle of metal, it is composed of three steps of recovery (removing internal stress of a structure strain-hardened through plastic working), recrystalization (generation of new crystal nucleus without internal stress), and growth (granular growth by combination of the new generated crystal nucleus and surrounding metal), and it takes aim at performing even recovery of removing internal stress that makes more movement difficult while maintaining the shape of strain hardening by plastic working.

[0119] In this case, recrystalization is generated over a heat treatment reference, the shape of the strain hardening is removed, so the high-strength functionality is lost.

[0120] The recovery heat treatment of the present disclosure is performed in a temperature range of 850~900°C for about 5 minutes in a continuous heat treatment furnace.

[0121] Unless specifically defined in the above description, all of technological and scientific terms used herein have the same meanings as those that are generally understood by those skilled in the art. Further, terms defined in common dictionaries are not construed ideally or excessively unless specifically clearly defined. Throughout the present specification, unless explicitly described otherwise, "comprising" any components will be understood to imply the inclusion of other components rather than the exclusion of any other components. Further, a singular form may include a plural form by the context.

[0122] The present disclosure is not limited to the exemplary embodiments described above and defined by claims, and it is apparent to those skilled in the art that the present disclosure may be modified in various ways without departing from the scope of the present disclosure described in claims.

[0123] The invention was made by the following national research and development projects.

[Project unique number] 1415181031
[Project number] 20020716
[Ministry] Ministry of Trade, Industry and Energy
[Project Management (Professional) Agency Name] Korea Institute of Industrial Technology Evaluation and Management
[Research project name]Development of Automotive Industry Technology
[Research project name]Development of Fuel Piping for Hydrogen Vehicle with Enhanced Deterioration of Water Resistance

Claims

1. A hydrogen fuel pipe for a hydrogen mobility, wherein

   an alloy material having a Ni equivalent (Ni_{eq}) 28.5% or more is configured by controlling the composition of C, Si, Mn, P, S, Ni, Cr, and Mo on the basis of 316-series stainless steel,
   a pipe is machined using the alloy material and has yield strength 75 ksi or more, tensile strength 105 ksi or more, and elongation 18% or more,
   a thickness Tm of the pipe is calculated by the following equation,
   allowable pressure is calculated 500bar or more,

$$T_m = \frac{D}{2}\,[1 - \exp(\frac{-1.155P}{S})]\ or\ P = \frac{S}{1.155}\ln[\frac{D}{D - 2T_m}]$$

where

$$Tm = \text{thickness x 0.9 (tolerance of 10\% applied)}$$

D = outer diameter
P = maximum allowable pressure

$$S = \text{allowable stress (yielded strength} \times (2/3))$$

a ratio of channel area/pipe area is calculated by the following equation,
when design pressure or use pressure of a pipe required by equipment or a facility at which the pipe is installed is 500~900bar, a ratio of channel area(inner area)/pipe area(outer area) of the pipe is 35% or more, and when design pressure or use pressure is 900~1200bar, the ratio of channel area(inner area)/pipe area(outer area) of the pipe is 25% or more.

$$\text{channel area(inner area)/pipe area(outer area)} = \pi\{(D-2 \times Tm)/2\}^2/\pi(D/2)^2$$

$$= (D - 2 \times Tm)^2/D^2$$

$$= \exp^2(-1.155P/S),$$

where

$$Tm = \text{thickness x 0.9 (tolerance of 10\% applied)}$$

D = outer diameter
P = maximum allowable pressure

$$S = \text{allowable stress (yielded strength} \times (2/3))$$

2. A hydrogen fuel pipe for a hydrogen mobility, wherein an alloy material having a Ni equivalent (Ni_{eq}) 28.5% or more is configured by controlling the composition of C, Si, Mn, P, S, Ni, Cr, and Mo on the basis of 316-series stainless steel,

yield strength is 55 ksi to less than 75 ksi, tensile strength is 100 ksi or more, and elongation is 25% or more,
a thickness Tm of the pipe is calculated by the following equation,
allowable pressure is calculated 500bar or more,

$$T_m = \frac{D}{2}\left[1 - \exp\left(\frac{-1.155P}{S}\right)\right] \text{ or } P = \frac{S}{1.155}\ln\left[\frac{D}{D - 2T_m}\right]$$

where

$$Tm = \text{thickness x 0.9 (tolerance of 10\% applied)}$$

D = outer diameter
P = maximum allowable pressure

$$S = \text{allowable stress (yielded strength} \times (2/3))$$

a ratio of channel area/pipe area is calculated by the following equation,
when design pressure or use pressure of a pipe required by equipment or a facility at which the pipe is installed is 500~900bar, a ratio of channel area(inner area)/pipe area(outer area) of the pipe is 35% or more, and
when design pressure or use pressure is 900~1200bar, the ratio of channel area(inner area)/pipe area(outer area) of the pipe is 25% or more.

$$\text{channel area(inner area)/pipe area(outer area)} = \pi\{(D-2 \text{ x } Tm)/2\}^2/\pi(D/2)^2$$

$$= (D - 2 \text{ x } Tm)^2/D^2$$

$$= \exp^2(-1.155P/S),$$

where

$$Tm \quad = \quad \text{thickness x } 0.9 \text{ (tolerance of 10\% applied)}$$

D = outer diameter
P = maximum allowable pressure

$$S \quad = \quad \text{allowable stress (yielded strength} \times (2/3))$$

3. The hydrogen fuel pipe of claim 1 or 2, wherein a pipe using the alloy material undergoes work hardening that includes pilger rolling and drawing processes and increases strength of a pipe, and then undergoes heat treatment.

4. The hydrogen fuel pipe of claim 1 or 2, wherein the pipe is a metal structure pipe composed of a recovery structure.

5. The hydrogen fuel pipe of claim 1 or 2, wherein the alloy material includes Mn of 1.6 to 2.00 wt%, Ni of 10.00 to 14.00 wt%, Cr of 16.00 to 18.00 wt%, and Mo of 2.0 to 3.0 wt%.

6. A member for a hydrogen mobility to which the hydrogen fuel pipe for a hydrogen mobility of claim 1 or 2 is applied.

7. A method of manufacturing the hydrogen fuel pipe for a hydrogen mobility of claim 1 or 2,

wherein an extruded mother material formed in a pipe shape and made of an alloy material having a Ni equivalent (Ni_{eq}) 28.5% or more by controlling the composition of C, Si, Mn, P, S, Ni, Cr, and Mo on the basis of 316-series stainless steel is prepared,
the alloy material includes Mn of 1.6 to 2.00 wt%, Ni of 10.00 to 14.00 wt%, Cr of 16.00 to 18.00 wt%, and Mo of 2.0 to 3.0 wt%,
a pipe cross-sectional thickness is reduced by performing pilger rolling on the mother material,
primary recrystalization heat treatment is performed on the obtained pipe,
the pipe cross-sectional thickness is reduced by performing primary cold drawing, secondary recrystalization heat treatment is performed on the obtained pipe,
the pipe cross-sectional thickness is reduced by performing secondary cold drawing, third recrystalization heat treatment is performed on the obtained pipe,
the pipe cross-sectional thickness is reduced by performing third cold drawing, and recovery and removal of magnetism (induced martensite) are achieved by performing recovery heat treatment in a temperature range in which induced martensite is removed and recrystalization is not generated.

8. The method of claim 7, wherein the primary, secondary, and third recrystalization heat treatment is performed at 1000 to 1200°C for 3 to 7 minutes, whereby annealing and solid solution heat treatment are performed.

9. The method of claim 7, wherein a cross-section reduction ratio of 71 to 73% is obtained by pilger rolling,

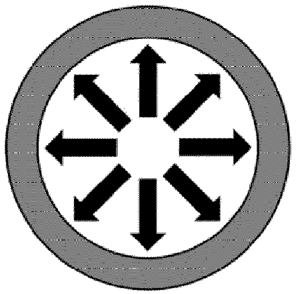
a cross-section reduction ratio of 32 to 34% is obtained by the primary cold drawing,
a cross-section reduction ratio of 33 to 35% is obtained by the secondary cold drawing, and
a cross-section reduction ratio of 38 to 40% is obtained by the third cold drawing.

10. The method of claim 7, wherein the recovery heat treatment is performed at 850 to 950°C for 3 to 7 minutes.

FIG. 1

EMBODIMENT 1 OF COMPONENT RANGE IN STANDARD; AND ALLOY DESIGN										
	%	C	Si	Mn	P	S	Ni	Cr	Mo	Ni eq.
316L BY ASTM (ASTM A213, A269)	Min						10.00	16.00	2.0	**22.36~31.5**
	Max	0.035	1.00	2.00	0.045	0.030	14.00	18.00	3.0	
CURRENT LEVEL OF DOMESTIC MOTHER PIPE	Ladle	0.019	0.337	0.745	0.027	0.004	12.133	16.498	2.03	**25.99**
ALLOY AIMING AT NICKEL EQUIVALENT OF 29% DESIGNED	Aim	0.010	0.40	1.60	0.030	0.008	13.20	17.50	2.6	**29.07**

FIG. 2



$$T_m = \frac{D}{2}\left[1 - exp\left(\frac{-1.155P}{S}\right)\right] \quad 또는 \quad P = \frac{S}{1.155}\ln\left[\frac{D}{D-2T_m}\right]$$

Tm = Thickness x 0.9 (Tolerance of 10% applied)
D = Outer diameter
P = Maximum allowable pressure
S = Allowable stress (yielded strength×2/3)

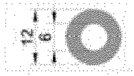
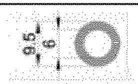
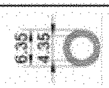
Example		Dimensions (Outer diameter × Inner diameter × **Thickness**)	Shape	Weight/1m	Lightweighting ratio	Flow rate	Specification (9 P Performance factors)			Allowable pressure
							Yield strength	Tensile strength	Elongation	
Commercial vehicle	**Conventional**	OD 12 x ID 6 x **WT 3**		677g	0%	Flow rate same	> 30 ksi	> 75 ksi	> 35 %	713 bar
	The invention	OD 9.5 x ID 6 x **WT 1.75**		340g	50%		> 75 ksi	> 105 ksi	> 25 %	1114 bar
Passenger vehicle	**Conventional**	OD 6.35 x ID 3.05 x **WT 1.65**		194g	0%	Increased 2 times	> 30 ksi	> 75 ksi	> 35 %	752 bar
	The invention	OD 6.35 x ID 4.35 x **WT 1**		134g	31%		> 75 ksi	> 105 ksi	> 25 %	994 bar

FIG. 3

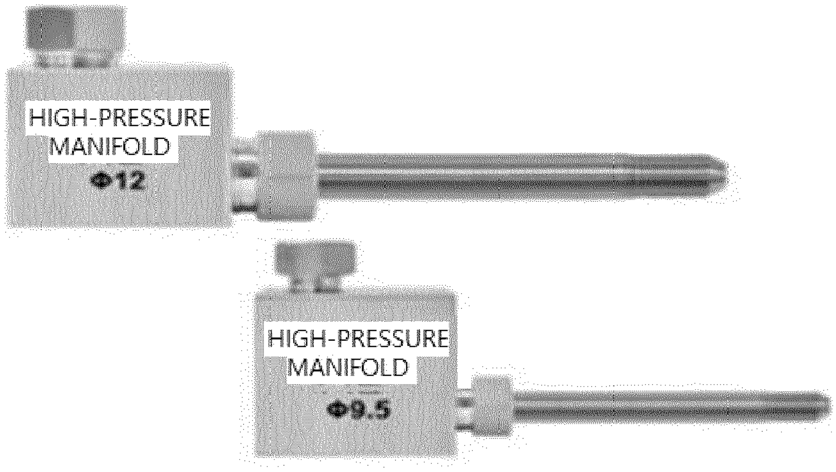


FIG. 4

PRODUCT	SIZE(Unit: mm)			PROCESS CONDITION			UNIT COST(Won/Kg)	THEORETICAL WEIGHT	UNIT COST (Won/6m)	EFFECT
	O.D	W.T	L	ROLLING	NUMBER OF TIMES OF DRAWING	HEAT TREATMENT				
EXISTING HEAVY PIPE	12.00	3	6,000	Cold Pilger	3 pass	Annealing	25,000	4.061	101,534	Effect of about **30% reduction** of unit cost of pipe part + **reduction of unit cost of fittings**
DEVELOPED LIGHT PIPE	9.50	1.75	6,000	Cold Pilger	**4 pass**	**High strength**	35,000	2.040	71,420	

FIG. 5

Outer diameter (mm)	Minimum thickness (mm)	Outer cross-sectional area (mm^2)	Inner cross-sectional area (mm^2)	Inner cross-sectional area/outer cross-sectional area	Remarks	Weight(kg)	Lightweighting
6.35	1.413	31.6531625	9.74858216	30.8%	YS 30ksi(Solid solution heat treatment) allowable pressure 700bar	0.174888	Reference
9.53	2.115	71.2944065	22.05065	30.9%	YS 30ksi(Solid solution heat treatment) allowable pressure 700bar	0.393166	Reference
12.7	2.817	126.61265	39.19375946	31.0%	YS 30ksi(Solid solution heat treatment) allowable pressure 700bar	0.697959	Reference
6.35	0.873	31.6531625	16.63950056	52.6%	YS 55ksi(Recovery heat treatment) allowable pressure 700bar	0.11987	Lightweighting of 30%
6.35	0.666	31.6531625	19.76655434	62.4%	YS 75ksi(Recovery heat treatment) allowable pressure 700bar	0.094904	Lightweighting of 45%
9.53	0.999	71.2944065	44.53385384	62.5%	YS 75ksi(Recovery heat treatment) allowable pressure 700bar	0.213658	Lightweighting of 45%
12.7	1.332	126.61265	79.06621736	62.4%	YS 75ksi(Recovery heat treatment) allowable pressure 700bar	0.379614	Lightweighting of 45%
6.35	1.863	31.6531625	5.40502016	17.1%	YS 30ksi(Solid solution heat treatment) allowable pressure 1050bar	0.209567	
6.35	0.945	31.6531625	15.614906	49.3%	YS 75ksi(Recovery heat treatment) allowable pressure 1050bar	0.128051	Lightweighting of 37% + pressure increase
6.35	1.215	31.6531625	12.062624	38.1%	YS 55ksi(Recovery heat treatment) allowable pressure 1050bar	0.156412	Lightweighting of 24% + pressure increase

FIG. 6

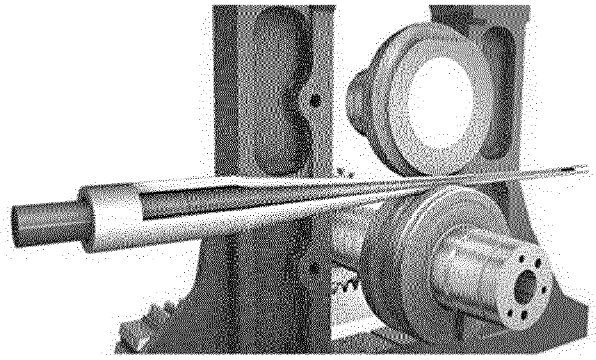


FIG 7

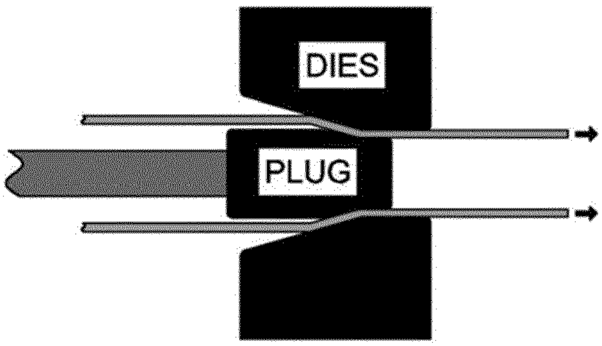


FIG. 8

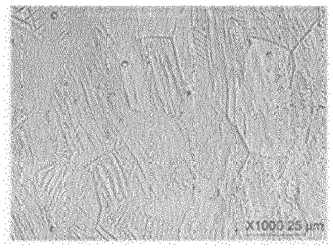


FIG. 9

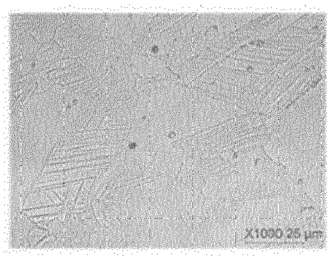
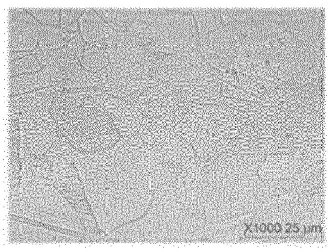


FIG. 10



REFERENCES CITED IN THE DESCRIPTION

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- Criteria for Selecting Materials to be Used for Hydrogen Station Equipment. **T. YAMADA ; H. KOBAYASHI.** J. High Press. Gas Saf. Inst. Japan. 2013, vol. 49, 885-893 **[0062]**
- **S. MATSUOKA ; J. YAMABE ; H. MATSUNAGA.** Criteria for determining hydrogen compatibility and the mechanisms for hydrogen-assisted, surface crack growth in austenitic stainless steels. *Eng. Fract. Mech.,* 2016, vol. 153, 103-127 **[0063]**