ABSTRACT

LNG storage and processing must first and above all be safe, and obviously also cost efficient. With the delivery of 9% Nickel for well over 150 storage tanks and other equipment and facilities worldwide, Industeel has developed a deep knowledge of the material and its implementation.

Based on that experience, Industeel has also developed solutions for other LNG related applications using adapted versions of that material or outright new concepts, to fill the need for optimal technical solutions for emerging technologies such as Cryogenic LNG Pipe Lines, Gravity Based Structures LNG storage, Floating LNG storage, High Pressure High Thickness Cryogenic LNG Processing Vessels and Equipments, Large Storage Spheres, Small Embarked LNG tanks for ship engine fuelling, small and mid-sized barge-based and land-based LNG tanks and shuttles.

The properties of the materials and the application-based challenges are presented and discussed in order to highlight the potential for use in new LNG projects.

INTRODUCTION

9% Nickel steel plate is the most common material used to construct the cryogenic containment system of onshore LNG storage tanks. As along its toughness at cryogenic temperatures, it also possesses both high strength and economical advantages, it can be considered as an interesting choice for newer concepts.

The metallurgy of that steel, its specificities and some comparisons with other materials are explained along with examples of use. Some of the features described herein are illustrated on the supporting poster available with the authors.

METALLURGY OF 9% NICKEL STEEL — MICROSTRUCTURE

9% Nickel steel is essentially martensitic steel, which in its quenched and tempered version can show that favourable microstructure up to high thicknesses like 100mm, useful in the pressure vessel fabrication range.

The know-how of the steel mill is important to avoid the development of possible other unfavourable microstructures detrimental in cryogenic service, such as ferrite-bainite.

The suitable fully martensitic microstructure evolves from a low carbon, nickel alloyed, material and is actually strong and tough, taking full use of its advantages and at the same time avoiding unwanted drawbacks. This structure is also devoid of meaningful austenitic phase so that the risk of fresh brittle martensite formation in service due to strains and stresses at low temperatures is avoided.

METALLURGY OF 9% NICKEL STEEL — CHEMISTRY AND CLEANLINESS

The plain steel as described in the standards is not sufficient to fully develop the intended properties of the material. In addition to these requirements, there is a need to limit the content of carbon and nitrogen-hardening elements - in order to avoid brittleness and enhance weldability. Typical carbon contents well
below 0.050wt-% have been found to give the best balance while average nitrogen contents largely below 50 ppm can be obtained with suitable under vacuum liquid metallurgy processing. The latter also helps to limit the presence of hydrogen in the metal.

An interesting side effect of the deep vacuum process is also that the long settling time helps potential inclusions to be removed from the matrix, leading to a clean and compact structure.

Brittleness at cryogenic temperature is also linked to tramp elements coming from the raw materials, which can be difficult to remove. Typical are lead, tin, antimony, bismuth, copper, sulphur and phosphorus. The best ultra low harmless levels needed are with typical phosphorus and sulphur contents below 50 and 10 ppm respectively, through a combination of optimised choice of raw materials with advanced liquid metallurgy practices. The Electric Arc Furnace route here has an advantage over the blast furnace plus basic oxygen metallurgy because it allows for a better control, first and foremost of the phosphorus content.

Special precautions must be taken during the continuous casting of the steel to mitigate segregation issues which could give rise to difficulties, for example in the T-shaped welded construction of the attachment of the circular plate ring on the bottom of the tank to the first shell as lamellar tearing could be feared to occur. Though-thickness “Z” direction reduction-of-area tensile tests have been conducted showing that results much better than 35% can be obtained, with typical values around 45%.

**METALLURGY OF 9% NICKEL STEEL MECHANICAL PROPERTIES**

Perfect management and control of the heat treatment sequence of quenching and tempering will give rise to the final mechanical properties of the material in a very reproducible manner. Typical tensile properties of about 700 MPa for the actual yield strength and of about 730 MPa for the actual ultimate tensile strength can be achieved over the whole range of fabricated thicknesses, which span from the 5mm typical of cylindrical tank bottom plates to the 60mm of some storage spheres pieces.

The achieved yield to tensile ratio of 9% Nickel steel is about 90% and over, and does not give rise to any brittleness in the metal thanks to the cleanliness of the steel that develops high ductility, making it able to undergo severe deformations without rupturing even at cryogenic temperatures.

The material is also very tough, with Charpy impact test results at -196°C of around 200J for the absorbed energy and 2mm for the lateral expansion, again largely beyond the codes and materials requisitions requirements and providing the steel with ample reserve towards an always possible lowering of properties linked to forming and welding, and hence against the risk of brittle fracture, therefore giving birth to very efficient designs and constructions.

Resistance against brittle fracture is further demonstrated by CTOD (Crack Tip Opening Displacement testing). Results at -165°C, the LNG temperature, of well above 0.50mm, including in the most critical heat affected zones of welds, are commonly achieved. This is linked to a very low stable residual austenite content which is more favourable in the intrinsic microstructural stability as the CTOD curves rarely - if ever - show any pop-in features. Extra confidence against brittle fracture propagation is evaluated with tests like the Pellini-type drop weight of PD7777 or the Duplex ESSO test and the capability of the 9% Nickel steel and its weld assemblies to withstand that test without problem up to 50mm - the thicker, the more demanding - has been already demonstrated for base materials, welds and heat affected zones.

A very low phosphorus content of the material, below 0.005%, is mandatory here to safeguard such features. This is important to notice because higher phosphorus levels up to about 0.008% see these safety properties being degraded while it cannot be easily observed in the more simple Charpy impact testing, as has been known for a long time. The authors are currently conducting a complete re-assessment of this sometimes forgotten dangerous phenomenon. Good historical discussions of this is however available and can for

**FABRICABILITY AND IMPLEMENTATION OF 9% NICKEL STEEL**

9% Nickel steel has a reputation of being difficult to handle. That steel is actually not really difficult to work with, but certainly needs know-how and clearly warrants trials and work sequence definitions like welding protocols. All competent fabricators, tank erectors, vessel makers, shipyards and welders are therefore able to handle it relying on their accumulated experience.

A typical large example of this, with a situation very similar to a Floating LNG (FLNG) storage tank, has occurred for the construction of the Adriatic LNG terminal. Some information on this project is available through its internet website http://www.adriaticlng.com and a detailed presentation was given by Lisa Waters et al. during the LNG15 conference in Barcelona in 2007, in paper PS6-7:

« Prior to starting work on the main tanks, the fabricator built an initial Fabrication Trial Structure (FTS), <...>. The primary fabrication challenge was associated with the distinct welding procedures, techniques and training required to successfully, efficiently and reliably weld 9% Nickel steel. Following on from the initial weld trials that confirmed parameters and production rates, a range of welding processes were used in fabricating the tank, including submerged arc, gas metal arc and shielded metal arc welding.<...> Additionally, special attention had to be paid to scheduling around the welding of the large volume of non-destructive testing that was specified. This included radiography, dye penetrant and ultrasonic examination. Magnetic particle inspection was not permitted due to the sensitivity of 9% Ni to magnetization and subsequent welding problems. This particular sensitivity to magnetization also meant that special care was required in handling and storage of approximately 11,000mt of 9%Ni plates as magnetic handling was not permitted and proximity to high voltage power lines had to be limited. »

Implementing 9% Nickel steel basically involved learning how to cut, handle, form and weld the material while avoiding practices that are unsuitable for this material.

Such improper practices are for example magnetic handling, because the steel remains highly magnetized which in turn gives rise to problems during welding, even when trying to circumvent this problem using demagnetization tools.

Another to-be-avoided practice is the “flame straightening” of plates because the Nickel alloyed steel grades can suffer from reversible temper embrittlement that can only be recovered by a full Post Weld Heat Treatment, generally impractical practice in shipyard configuration. This is true even with very low phosphorus contents even though the latter is obviously helpful for that matter. Teaching the welders the good practices is fairly common with welding consumable suppliers and experienced steelmakers, as the weld metals are often nickel-based alloys that need some training.

**ADVANTAGES OF 9% NICKEL STEEL OVER OTHER CRYOGENIC SERVICE METALLIC MATERIALS**

The actual yield strength of 9% Nickel steel is typically 3 times that of austenitic stainless steel whereas its tensile strength is 50% higher. Even taking the specified values, this allows for a meaningful reduction of section in certain places, leading to a very interesting economy of weight and all the collateral advantages this may bring.
Table I illustrates a typical comparison that can be made between some cryogenic materials in terms of nominal properties.

Table I. Physical properties and features of several cryogenic materials, showing the favourable positioning of 9% nickel steel.

Of notice not illustrated here is also the elastic modulus (Young’s modulus) of Al alloys that are typically three times lower than those of steels, thereby rising concerns for structures where buckling is a risk.

<table>
<thead>
<tr>
<th>Material property</th>
<th>9% Nickel steel</th>
<th>SS type 304L</th>
<th>SS type 304N</th>
<th>36%Ni “Invar”</th>
<th>Al-Mg 5083 0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal Minimum Yield Strength (MPa)</td>
<td>585</td>
<td>205</td>
<td>240</td>
<td>240</td>
<td>160</td>
</tr>
<tr>
<td>Nominal Minimum Tensile Strength (MPa)</td>
<td>690</td>
<td>515</td>
<td>550</td>
<td>450</td>
<td>270</td>
</tr>
<tr>
<td>Nominal Minimum Elongation at rupture (%)</td>
<td>20</td>
<td>40</td>
<td>30</td>
<td>40</td>
<td>30</td>
</tr>
<tr>
<td>Linear thermal expansion ratio (10^-6.K^-1)</td>
<td>9</td>
<td>18</td>
<td>18</td>
<td>2</td>
<td>24</td>
</tr>
<tr>
<td>Thermal conductivity ratio (W.m^-1.K^-1)</td>
<td>30</td>
<td>16</td>
<td>16</td>
<td>16</td>
<td>118</td>
</tr>
<tr>
<td>specific weight (kg.m^-3)</td>
<td>7850</td>
<td>7900</td>
<td>7900</td>
<td>8000</td>
<td>2660</td>
</tr>
</tbody>
</table>

The actual tensile properties of 9% Nickel steel being higher than those required by the standards, it has been suggested to use this in calculation codes, but such considerations – while interesting in terms of economies of design - are still in a very early stage of development.

An additional advantage of 9% Nickel steel over its competitive materials is that the plates are generally available in larger dimensions, thereby possibly allowing for a minimization of the quantity of welds that have to be produced to build the equipment.

But one of its most striking features is the balance of physical properties given by the 9% Nickel steel versus austenitic stainless steels like 304L under application conditions, where for example the limited coefficient of thermal expansion (CTE) of the martensitic material helps in limiting reinforcement needs due to the shrinkage of the structure in operation and the associated extra stress on the material. It is also to be noticed that this CTE of 9% Nickel is the same as those of structural steels, thereby enhancing the appropriateness of the mechanical linkage between cryogenic and ambient environments, like in the cases of FLNG tanks or cryogenic pipes. The thermal conductivity of 9% Nickel is also much higher than that of 304L, meaning that cooling is easier and less thermal gradients are susceptible to appear in service.

APPLICATIONS OF 9% NICKEL STEEL

The material is well known for its suitability to contain LNG in medium to large storage atmospheric pressure storage tanks, typically from 70,000 to 180,000 cubic metres capacity in a cylindrical vertical configuration. Its high strength however has also made it the material of choice for warmer cryogenic storage applications even at smaller volumes. Liquid ethylene tanks come here in the first place of existing alternate uses.

Very large onshore LNG storage tanks, above 200,000 cubic meters of capacity and capable of replacing two or more smaller tanks with a lesser ground plot, can be built using the thicker plates that are now available. Those thicker plates, above 50mm, are also of interest in the construction of optimized cryogenic storage spheres where their strength and relative ease of implementation lead to such weight gains that this more than counterbalances the potentially higher alloy cost.

9% Nickel steel can also be used for the cryogenic tanks of Floating LNG platforms (FLNG), as experience exists on a similar kind of shipyard-like construction for the Adriatic LNG GBS terminal as described before. Developments of FLNG concepts effectively raise a question on the design of the storage tanks because of
the potentially dangerous effect of sloshing on the integrity of some softer, non-structural, ship storage tank designs at medium filling levels.

9% Nickel steel can in addition help limit the deadweight of the vessel compared to concurrent materials by minimizing the thickness needed in some topside equipment.

9% Nickel steel is also an interesting option to optimize cryogenic piping systems in its ability to reduce considerably the need for expansion loops thanks to its favourable thermal expansion coefficient and cost positioning versus competitive options.

9% Nickel steel can also be readily applied for the smaller LNG tankage needed aboard ships that can be fuelled with it, as well as bunkering stations in the ports.

CONCLUSIONS

Enabling technologies for new LNG concepts include a suitable choice of materials of construction. Experience in production of 9% Nickel steel has permitted development well further than the minimum requirements of standards. This allows not only for safe current designs but also for very large and very small LNG tanks, FLNG storage tanks, more efficient cryogenic pipes, and lighter cryogenic pressure equipment. This contributes from the backstage to the actual feasibility of newer concepts.

9% Nickel steel is intrinsically a difficult grade to make, since several difficulties must be overcome in the steelmaking and in the rolling and finishing of the plates. It takes a specialized and experienced steel mill with continued deliveries and committed to supply the market demand to achieve suitable properties including in the non-explicit aspects of the fabricator and end-users needs, for example the mitigation of embrittlement risks of heat affected zones of weldments during the ageing of the facilities through a drastic limitation of the phosphorus content of the steel.