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Properties of Metallic Materials for LNG Service

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ABSTRACT

This paper presents the key physical and mechanical properties of 9% Ni steel, AISI 304L stainless steel, 36% Ni low expansion alloy and aluminium alloys which are all used for low temperature engineering, specifically for the handling of liquefied natural gas (LNG). Typical values for all key properties are given. A theoretical explanation is given for why the alloys have certain properties, particularly covering the origin of toughness in different kinds of crystal structures, and also explaining the phenomenon of the interaction of magnetic properties and thermal expansion which results in the low expansion coefficient of the 36% Ni material. Practical information on the use and fabrication of the alloys is included.

1. INTRODUCTION

Engineering systems for handling liquefied natural gas are designed for an operating temperature of –163°C. Metals for use at such cryogenic temperatures have to comply with exacting demands with respect to their mechanical and physical properties. The tensile strength of metals tends to increase at lower temperature. Metals have to have sufficient strength in service, but also have to be strong enough to be formed and fabricated at ambient temperature. In terms of mechanical properties, the need for adequate toughness is of primary concern. Whether a metal is tough at a given temperature depends upon whether it is able to plastically deform and that depends directly upon the crystal structure of the metal. This issue is described in more detail below.

The physical properties, such as the thermal conductivity, also have to be considered in the design. The value of the coefficient of expansion will influence the amount of thermal strain induced during cooling to the operating temperature and this influences the detailed design approach for various components.

The aim of this paper is to present certain metal properties pertinent to low temperature application and to give some of the theoretical background to explain the properties. The paper draws together many of the critical properties to provide a useful reference resource for design engineers and metallurgists.

2. CRYSTALLOGRAPHIC NATURE OF PLASTIC DEFORMATION

In considering metals, that are suitable for pressure containment at -163°C, the key property that limits the application of many of the most common metals (including most steels) at such temperatures is toughness. Toughness is the ability of a metal to deform in a ductile, rather than brittle, manner when exposed to loads or strains with decreasing temperature. Toughness can be measured using compact tension and crack-tip opening displacement testing at slow strain rates or by Charpy testing at high strain rates (impact loading).

It can be shown theoretically that to get ductile behaviour in toughness tests a metal has to have 5 active slip systems. Face centred cubic (f.c.c.) metals, such as nickel and aluminium have a total of twelve possible slip systems which can take part in the deformation. Moreover, this behaviour persists in solid solutions with f.c.c. structure (i.e. alloys behave in a similar way to pure single metal systems). It is this fundamental existence of a multiplicity of slip systems, each of which offers a low shear stress limit (just about 11 MPa for nickel), which means that f.c.c. materials behave in an inherently ductile fashion. Face centred cubic crystals do not show brittle behaviour. They do not show a ductile to brittle transition with temperature and are fully ductile over the full temperature range.

The other main crystal structure is the body centred cubic (b.c.c.) structure which is found in iron (typical carbon steel structure). However, at lower temperatures (below the transition temperature), there are typically only two or three slip systems available in b.c.c. metals and they are therefore brittle.

The great benefit in toughness properties of the f.c.c. crystal structure is exploited in the 9Ni steels. These steels contain sufficient nickel so that the microstructure consists of the normal ferritic (b.c.c.) crystals, or grains, with a small proportion of fully austenitic (f.c.c.) grains. Whilst the volume fraction of austenite is fairly small (about 4%), it is sufficient to ensure that the steel has a high toughness even at –163°C.

3. METALS FOR APPLICATION AT CRYOGENIC TEMPERATURE

There are four metals practically established in various applications for handling LNG. These are listed in Table 1 along with examples of components required in LNG systems.

3.1. Chemical Composition

Typical chemical compositions of the metals used in LNG systems are given in Table 2.

3.2. Heat Treatment Condition

A list of the typical standards for 9Ni steel is given in Table 3. These show that 9Ni steel can be used in two standard heat treatment conditions: Quenched and Tempered (QT) and Double Normalised and Tempered (NNT). The metallographic structures usually formed in the steel after water quenching or air cooling from the austenitising temperature (around 800ºC) are martensite or bainite with a maximum hardness dependent on the carbon content but rarely more than 400 HV. The final tempering treatment heats the steel just above the austenite reformation temperature (around 580°C) to reform a small amount of austenite. This tempers the martensite and the carbon diffuses into the small austenite grains to stabilise them. After final tempering the microstructure consists of ferrite with a fine distribution of carbides and approximately 4 vol% retained austenite. This results in a steel of high strength and excellent toughness.

The QT route tends to produce a steel with higher yield strength (YS) and high yield strength to tensile strength (YS:TS) ratio. The choice of heat treatment route depends principally upon the choice of design code. Where a TS-based design code is chosen there is little incentive to select the QT grade. The opposite is true where a YS based design code is used. In that case there is also incentive to select high yield strength weld consumables, even if there is a cost penalty.

The other alloys (304L, 36NiFe and Al alloys) are used in the annealed condition with all the alloying elements in solution. They do not require further heat treatment prior to fabrication. In fact heating below the annealing temperature can be detrimental to stainless steels if it is prolonged sufficiently to cause chromium carbide precipitation. The microstructure is then 'sensitised' and has reduced corrosion resistance. Similarly, aluminium alloy 5083 should not be subjected to heating below the annealing temperature as Mg_5Al_3 or Mg_5Al_8 precipitates can form with resulting risk of stress corrosion cracking.

3.3. Physical Properties

Some physical properties of the metals used for LNG handling are presented in Table 4.

The remarkably low coefficient of expansion of 36NiFe arises because of the superposition of two phenomena, one related to thermal expansion and the other related to the ferromagnetic-paramagnetic transformation. Charles-Edouard Guillaume was awarded the Nobel Prize in 1920 for his discovery of, and explanation of, the low coefficient of expansion of 36NiFe alloy. He observed the contraction of this alloy on cooling and found that its length remained virtually unchanged when cooling from the Curie Point (the temperature corresponding to the paramagnetic-ferromagnetic transformation, about 260ºC for this alloy). The change in length was least when the rate of change of magnetic transformation from para- to ferro- magnetic behaviour was at a maximum[1]. The increase in ferromagnetism at lower temperatures results in an increase in atomic spacing, which counteracts the normal contraction due to the reducing temperature.

The thermal conductivity of the aluminium alloy is very much higher than the other materials. This is advantageous for its use for a cryogenic heat exchanger.

The varying physical properties of the different alloys result in differing levels of thermal stress as the metals cool. The last rows of Table 4 calculate an approximate stress level for the contraction of a restrained length of metal from zero to –163ºC. The thermal stress, $\sigma = E\varepsilon = E\,\alpha\,\Delta T = 163\,E\,\alpha$, where E is the Young's Modulus, ε is the strain, α is the coefficient of expansion and ΔT the temperature range. The absolute value is given in MPa and the value as a percentage of the minimum yield strength (from Table 5).

The stress is lowest in 36NiFe because of its extremely low coefficient of expansion. Whilst the stress is high in 9Ni, its high strength prevents this alloy from yielding because of the thermal strain of contraction. The low Young's modulus of the aluminium alloy keeps the stress fairly low but still above the yield strength of the alloy. The high elastic modulus and expansion coefficient of the stainless steel result in the highest stress levels, also well above the yield strength of the material. As a result of the physical properties, both stainless steels and aluminium alloys have to be designed with expansion loops or with structures of inherently low modulus (such as the 'waffle' design of membrane used for the stainless steel tanks) in order to keep the contraction stresses below yield value.

3.4. Mechanical Properties

The mechanical properties of the metals used for LNG handling are presented in Table 5.

Most mechanical properties are taken from typical values for annealed material. In some cases different sources give different values. In such cases the mid-range of values is reported here. Specified minimum values at room temperature vary depending upon the specification but are generally much lower normal values in terms of strength, toughness etc.

The rise in strength which is noted in the 304L stainless steel and 36NiFe alloy as the temperature drops are a result of the effect of interstitial elements (typically nitrogen or carbon) in the crystal lattice as it cools down. The aluminium alloy does not have any interstitial alloying elements (all elements are fully dissolved) and so there is little change in the strength as the temperature drops from zero.

The aluminium alloy shows low Charpy Impact toughness values in the parent metal, with almost identical values also found in the weld zone, and little change in cooling to cryogenic temperature. This reflects the low shear strength of this alloy.

A potential factor to consider in the case of type 304L stainless steel and 36NiFe would be the stability over long period to exposure to temperatures of -163°C as some metals can undergo (partial) transformation to martensite at these temperatures. This is a strong microstructural constituent but it tends to reduce the metal ductility and toughness. However, long term past performance of these materials in cryogenic applications indicates that this is not a practical concern.

3.5. Fabrication Aspects

The different metals are available in different forms (Table 6). 9Ni steel is made only as plate, geared to its main application for storage tanks. In some cases it has been formed into pipe and longitudinally welded but this product form is not often used.

The other alloys are available as plate or as strip, which is easily formed into tubing or pipe.

Welding of stainless steels and 9Ni steel is described in detail elsewhere[2,3]. Some general points are described below.

3.5.1. 9Ni steel can be prepared for welding by flame cutting and grinding. Weld preparations need to be slightly wider than for conventional steels to ensure good root access. Welding methods used include GMAW, GTAW and SMAW, although some fabricators have used SAW. The strong magnetic nature of 9Ni can lead to problems of arc blow, which can be minimised by avoiding direct current welding and by de-magnetising on site. Pre-heating of the weld zone is not necessary. The maximum interpass temperature is 150ºC.

Three categories of welding electrode can be used[4]:

1) Ni/15-22Cr/ Fe type with additions of Mo, Nb etc.
2) 50Ni/13Cr/Fe/Mo type

3) 16Cr/13Ni/Mn/W modified austenitic type

The weld consumable usually selected is the first type, Ni 22Cr 9Mo 3.5Nb (Alloy 625), which gives an as-deposited yield strength of about 450 MPa and tensile strength of about 700-800 MPa minimum. Because the weld metal is slightly undermatching the parent metal in strength, the wall thickness of the tanks is usually increased to compensate. Nevertheless, cross-weld tensile specimens tend to yield first in the gauge region, and then work –harden, with ultimate yielding in the surrounding parent metal once the TS of the work hardened weld has exceeded the parent steel yield strength. The normally applied design guides tend not to exploit the tensile properties of the weld region to the full.

There is a tendency for the HAZ to show higher hardness than the weld deposit but the hardness can be controlled by limiting the parent metal carbon content to 0.08% max. With that carbon level the maximum hardness falls below 350Hv and so no post-welding stress relief heat treatment is required.

The very fine microstructure in the HAZ results in good toughness with Charpy impact values throughout the weld zone tending to be in excess of 100J at –196°C. Extensive critical defect length tests have been carried out on 9Ni structures indicating quite long critical defect sizes (dependent upon the precise crack tip location) typically between 19-47 mm. Tests with pre-existing defects have proven that 9Ni tanks will leak-before-break. Decommissioned 9Ni tanks have also been extensively inspected after many years in service, and show no deterioration in properties or tendency for slow crack extension[5,6].

3.5.2. Welding of stainless steels for LNG service requires the same weld preparation and controls as would be found for any conventional stainless steel welding. Many welding techniques are applied, although there is a preference for GTAW for thin sections. The welding consumables selected for 304L stainless steel are E308L (rod) and ER 308L (wire), with adjusted chemical compositions for 'Low Temperature' application.

The key difference in welding procedures, compared to fabrication of stainless steels for use at ambient conditions, is to aim for a low volume of delta ferrite in the weld. Whereas conventional welding would allow 5-12% delta ferrite (to assist in reducing hot cracking), it is normal practice for LNG service to limit the ferrite to lower values (0-2 Ferrite Number according to IIW Document II-C-871-91) in order to maximise the toughness. Resistance to hot cracking in these low ferrite welds depends upon keeping the S and P to a minimum in the weld consumable and having sufficient Mn to react with the S to form MnS inclusions.

Weld toughness is also optimised by keeping the weld oxygen content low (e.g. basic rather than rutile coated electrodes) and nitrogen content low e.g. by good gas shielding with Ar or Ar-He mixtures. Minor additions of CO_2 or O_2 may be used in GMAW shielding gas to improve the arc characteristics.

The presence of some delta ferrite in the weld zone increases the strength relative to the parent metal and reduces the toughness.

3.5.3. 36NiFe is normally in the form of thin sheets and is generally welded by GTAW. The 'matching' filler wire has very low levels of trace elements (S, P, Al, B, N) to minimise porosity and re-heat cracking. The wire is also alloyed with 0.5-1.0% Ti and up to 3% Mn which react with contaminant elements to form inclusions. These help to nucleate a fine dendrite structure in the weld zone. Alternatively 36NiFe can be welded by resistance seam welding without any filler material. This welding technique has been applied for the fabrication of LNG containment tanks made with the membrane design.

No pre- or post- welding heat treatment is used. Surfaces should be clean before welding and any oxidation removed by grinding. The heat input should be kept low with a low interpass temperature of 180°C to prevent any grain growth in the weld or HAZ.

3.5.4. Aluminium alloys are welded using gas shielded processes (GTAW and GMAW) with Ar or Ar-He gas. Filler metals for welding alloy 5083 include 5183, 5356 and 5556A. The welds have tensile and toughness properties very similar to the parent metal, both at ambient and cryogenic temperature.

Where the 6000 series of alloys are selected (e.g. for flanges) suitable filler metals include the Al-Si grades which are resistant to weld metal solidification and HAZ liquation cracking, or Al-Mg filler metals which produce more ductile welds. These alloys show a loss in strength of the HAZ after welding. Whilst this can be recovered by heat treatment, that is rarely practicable and so the allowable design stress for welded 6000 series has to be reduced to account for the loss in strength on welding.

4. CONCLUSIONS

A range of alloys, 9% Ni steel, AISI 304L, 36% NiFe and Aluminium alloys, with diverse mechanical and physical properties has been applied for handling liquefied natural gas since the start of the LNG business over the last 40 years. Certain specific properties have been shown to derive fundamentally from the atomic and crystalline structure of the metals concerned which thus limits the number of suitable alloys for LNG applications. Correct use of these alloys, allowing for the impact of their specific properties on the design, allows the correct material to be used for each application.

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Table 1 – Typical Applications of Metals Used for LNG Systems

Alloy	TYPE	APPLICATION
9Ni	9% Ni steel	Storage tanks
304L	Stainless steel type AISI 304L	Piping; Small vessels. Some designs of large storage tanks.
36NiFe	Low expansion, 36%Ni-Fe alloy	Some large storage tank designs. Piping in critical applications.
Al	Aluminium alloy type 5083 (Al-4.5%Mg) Alloy 5154 (Al-3.5%Mg) Alloy 6000 (Al –Si)	Spherical or prismatic storage tanks for ship transportation of LNG. Tubing for the main cryogenic heat exchanger. Forgings such as flanges.

Table 2: Typical Chemical Compositions of Metals Used in LNG Systems.

		Element (Maximum weight%)											
Alloy	UNS	C	Si	Mn	S	P	Ni	Cr	Fe	Al	Cu	Mg	Zn
9Ni	K81340	0.13*	0.15-0.35	1.00	0.040	0.035	8.00-10.00	-	Bal	-	-	-	-
304L	S30403	0.03	1.00	2.00	0.030	0.040	8.0-12.0	18.0-20.0	Bal	-	-	-	-
36Ni	K93600	0.04	0.25	0.2-0.4	0.012	0.012	35-36.5	-	Bal	-	-	-	-
Al 5083	A95083	-	0.40	0.40-1.0	-	-	-	0.05-0.25	0.40	Bal	0.10	4.0-4.9	0.25
Al 6061	A96061	-	0.40-0.8	0.15 max.	-	-	-	0.04-0.35	0.7 max.	Bal	0.15-0.40	0.8-1.2	-

* lower carbon content, e.g. 0.04 - 0.08%, reduces the risk of excessive HAZ hardening.

Table 3 – Specifications for 9Ni steel Indicating Heat treatment Conditions Covered

Country	Specification	Heat Treatment Condition
Belgium	NBN 630-70	
France	AFNOR A36-208	
Germany	Werkstoffblatt 680-70	NNT or QT
Italy	UNI 5920-66	NNT or QT
UK	BS1501 – 509 BS1501-510	NNT or QT QT
USA	ASTM A353 ASTM A553	NNT QT

NNT = Double normalised and Tempered
QT = Quenched and Tempered

Table 4 – Physical Properties of Metals Used for LNG Systems

Property	T °C	9%Ni Steel	AISI 304L Stainless Steel	36% Ni Fe Alloy	Al alloy 5083
Density, kg/m^3		7860	7900	8120	2660
Elastic Modulus E, GPa	+20 -196	186 207	193 205	148 138	70 81
Thermal Conductivity, W/m°C	+20 -196	28.5 13.0	13.4-15.1 9	10.5 5.7	117
Mean Coefficient of thermal expansion, α, 10^{-6}/°C	0 to -196	9.5	14.4 – 15 (at 0°C) 11.7 - 13.5 (at -196°C)	1.5	17.5
Theoretical thermal stress in contracting a rigid length from 0 to -163°C, MPa $\sigma = E\varepsilon = E\,\alpha\,\Delta T = 163\,E\,\alpha$		304	440	34	228
Theoretical thermal stress in contracting a rigid length from 0 to -163°C, MPa as a percentage of yield strength		51-69%	176%	12.6%	157%

Table 5 – Mechanical Properties of Metals Used for LNG Systems (Typical values unless stated to be 'specified')

Property	T °C	9%Ni Steel	AISI 304L Stainless Steel	36% Ni Fe Alloy	Al alloy 5083
Yield stress, MPa	0	441-587 min. specified 650 (NNT), 690 (QT)	250	270	145
	-196	680 (NNT), 840 (QT)	400	650	165
Ultimate tensile stress, MPa	0	637-834 min. specified 840 (NNT)	590	490	290
	-196	1100 (NNT), 940 (QT)	1525	900	405
Elongation to break, %	0	17-20 min.specified 30	60	40	16
	-196	23	40	40	36
Impact energy, J	0	125	200	150	24[7]
	-196	42	100-150 parent 70-90 HAZ 50-70 GMAW 40-100 SMAW	>100	20

Table 6 – Fabrication Aspects of Metals Used for LNG Systems

	9%Ni Steel	AISI 304L Stainless Steel	36% Ni Fe Alloy	Al alloy 5083
Availability in: - thin sheet, strip - plate - tube - bar/rod - wire	 No Yes No No No	 Yes Yes Yes Yes Yes	 Yes No No Yes Yes	 Yes Yes Yes Yes No
Welding methods*	GMAW, SMAW, GTAW, SAW	GTAW or GMAW	Resistance seam welding or GTAW	GTAW or GMAW
Welding consumable	70Ni type (alloy 625) 50Ni type 16Cr type	Use 308L stainless steel electrodes giving max. ferrite number 2 in the weld zone	Use filler with 0.5-1.0%Ti and up to 3%Mn	Alloys 5183, 5356, 5556A

* GTAW = Gas Tungsten Arc Welding
GMAW = Gas Metal Arc Welding
SMAW = Shielded Metal Arc Welding
SAW = Submerged Arc Welding