PRODUCTION AND PROPERTIES OF HIGH-STRENGTH NICKEL-ALLOY STEEL PLATES FOR LOW TEMPERATURE APPLICATIONS

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ABSTRACT

Liquefied natural gas is usually transported by specially equipped ships and stored in LNG terminals. The construction of vessels and tanks for LNG/LEG transportation purposes leads to a demand for steels with specified low temperature properties.

This article gives an overview on the production, properties and processing behaviour of 5% and 9%-nickel-alloyed high-strength steels for low temperature applications produced by ThyssenKrupp. Further an insight into industrial production experience and an illustration of the application of nickel steel plates in projects around the world is given.

KEYWORDS

5% nickel-alloyed steel, 9% nickel-alloyed steel, Production route, Material properties, Cryogenic Applications, LNG Storage,

INTRODUCTION

While consumption of energy in the world is rising there is growing interest in the use of gas, especially natural gas as a source of energy. The world´s largest gas resources are, however, generally located far away from the main areas of consumption. This leads to the need for storage and long distance transportation of huge amounts of gas.

In this context liquefying the gas is of major interest because by liquefaction it´s volume can be reduced by a factor of up to 600 which obviously simplifies storage and transportation and means significant cost reduction. Due to physical reasons temperatures for liquefying commonly used types of gas are below –100 °C. Relevant temperatures are approx. –162 °C for liquefied natural gas and approx. –104 °C for liquefied ethylene gas (LEG).

Liquefied natural gas (LNG) from overseas is usually transported by specially equipped ships and stored in LNG-terminals [1,2]. LNG-terminals with great storage capacity are constructed as flat bottom tanks according to technical rules like EEMUA, API 620, BS 7777 (**Fig. 1a**). Here three different principles of construction are available:

- Single containment
  (self-supporting inner wall of nickel-alloyed steel/insulation/outer wall of structural steel + dike)
- Double containment
  (single containment + outer wall of pre-stressed concrete; dike not necessary)
- Full containment
  (double containment + concrete roof + sealing between inner and outer tank)

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Frequently the tanks are coated still with a concrete-wrapper. For transportation with LNG tankers on which the gas is stored mostly in spherical tanks are used (**Fig. 1b**).

b)

a)

Fig. 1: Application of high-strength nickel-alloyed steels

The construction of vessels and tanks within the typical LNG-chain leads to a demand for steels with specified low temperature properties. Because of the high danger potential material requirements are exceptionally high. The steels need to remain ductile and crack resistant with a high level of safety even at the mentioned low temperatures. The deployed steels must also have high strength in order to allow reduction of wall thickness of tanks which permits economic favorably construction. Beyond that, welding without any risk of brittle fracture is of importance. According to these demands high-strength steels with remarkable amounts of Ni (5 to 9%) are well established. The **Fig. 2** shows different kinds of raw material with corresponding working temperatures and the type of steel and Ni-content, suitable for this application. From this, it is evident, that for highest demands on low temperature service, i.e. for LNG-applications, steels with 9% Ni stand in the foreground.

Stored/Transported Gas	Boiling Point [°C]	Identification	Used Steel Grade
Butane	-0.5	Liquefied Petroleum Gas (LPG)	Fine Grained Steels
Propane	-42		
Carbon Dioxide	-78		1,5 % Nickel Steels
Ethane	-89		3,5 % Nickel Steels
Ethylene	-104	Liquefied Ethylene Gas (LEG)	5 % Nickel Steels
Methane	-162	Liquefied Natural Gas (LNG)	9 % Nickel Steels
Oxigen	-183		
Argon	-186		
Nitrogen	-196		

Fig. 2: Liquefaction temperatures of gases and types of parent materials

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1. MATERIALS FOR LOW TEMPERATURE APPLICATIONS

Nickel alloy steels, especially with 9% nickel content, meet high requirements concerning toughness at low temperatures and provide a good combination of the demanded properties. These excellent toughness properties are the result of an optimized microstructure containing fine grained martensite with high Ni-content. The Ni-alloyed high-strength steels are delivered in accordance with different specifications.

Fig. 3 gives an overview on the specified steel grades, their chemical composition and the required mechanical properties [3, 4]. High-strength steels with 5% or 9% Ni are preferably delivered according to DIN EN 10028-4 as X12Ni5 or X7Ni9 (X8Ni9) or according to ASTM/ASME-Standard as A553 Type I. The nickel-alloyed steels exhibit a low carbon content below 0,15% and a Mn-content below 0,80%. Additionally the alloying of max. 0,10% Mo is possible for grade X7Ni9/X8Ni9. It is important to point out, that in both rules the heat treatment conditions are specified.

<table>
<tr><th rowspan="3">Standard</th><th rowspan="3">Steel Grade</th><th rowspan="3">Type</th><th rowspan="2">Plate Thickness</th><th colspan="8">Heat Analysis</th><th colspan="3">Tensile Test</th><th colspan="2">Charpy V (transv.)</th><th>Lateral Expansion</th></tr>
<tr><th>C</th><th>Si</th><th>Mn</th><th>P</th><th>S</th><th>Mo</th><th>Ni</th><th>V</th><th>R_e</th><th>R_m</th><th>A</th><th>-120 °C*</th><th>-196 °C</th><th>-196 °C</th></tr>
<tr><th>mm</th><th colspan="8">%</th><th colspan="2">MPa</th><th>%</th><th colspan="2">J</th><th>mm</th></tr>
<tr><td rowspan="4">EN 10028-4</td><td>X12Ni5</td><td></td><td>≤30
>30≤50</td><td>≤,15</td><td>≤,35</td><td>,30
to
,80</td><td><,020</td><td><,010</td><td></td><td>4,75
to
5,25</td><td>≤,05</td><td>≥390
≥380</td><td>530 to 710</td><td>≥20</td><td>≥27</td><td></td><td rowspan="4"></td></tr>
<tr><td rowspan="2">X8Ni9</td><td>QT 640</td><td>≤30
>30≤50</td><td rowspan="3">≤,10</td><td rowspan="3">≤,35</td><td rowspan="3">,30
to
,80</td><td rowspan="2">≤,020</td><td rowspan="2">≤,010</td><td rowspan="3">≤,10</td><td rowspan="3">8,50
to
10,00</td><td rowspan="2">≤,05</td><td>≥490
≥480</td><td>640 to 840</td><td rowspan="3">≥18</td><td rowspan="3"></td><td>≥40</td></tr>
<tr><td>QT 680</td><td>≤30
>30≤50</td><td>≥585
≥575</td><td rowspan="2">680 to 820</td><td>≥50</td></tr>
<tr><td>X7Ni9</td><td></td><td>≤30
>30≤50</td><td>≤,015</td><td>≤,005</td><td>≤,01</td><td>≥585
≥575</td><td>≥80</td></tr>
<tr><td>ASTM
ASME</td><td>A 553
SA 553</td><td>Type I</td><td>≤50</td><td>≤,13</td><td>0,15
to
0,40</td><td>≤,90</td><td>≤,035</td><td>≤,035</td><td></td><td>8,50
to
9,50</td><td></td><td>≥585</td><td>690
to
825</td><td>≥20</td><td></td><td></td><td>≥0,38</td></tr>
</table>

* test temperature is -110 °C for plate thickness t ≤25 mm and -115 °C for 25 mm <t ≤30 mm

Fig. 3: International Standards for 5% and 9% Ni-steels

For safety reasons resistance against brittle fracture is of major importance for steels employed in constructions for LNG-applications. Therefore toughness requirements for impact testing have increased over the last decades. In most cases requirements exceed the minimum values determined in the standards mentioned above. **Fig. 4** gives an overview on the evolution of toughness requirements for 9% nickel-alloyed steels (test temperature: –196 °C). It is illustrated that today´s demands for minimum toughness values up to 100 J exceed values demanded 30 years ago by factor 3. To satisfy highest demands on toughness special heat treatment procedures are applied.

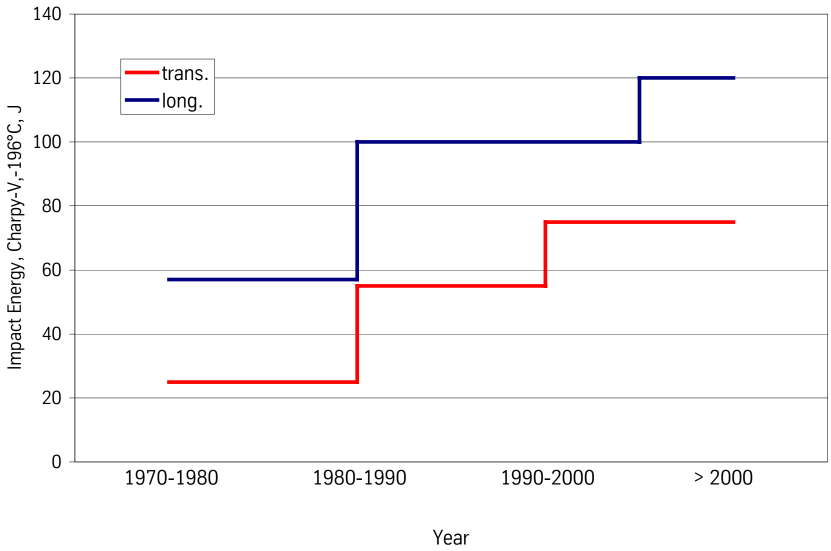

Fig. 4: Development of requirements for minimum impact toughness of 9% Ni-steels

2. PRODUCTION OF HIGH-STRENGTH NI-ALLOYED STEEL

Pre-condition for the production of steel products which are raked to the demands of the market in full extent was progress in metallurgy, rolling and heat treatment technique. In the steel works of ThyssenKrupp Steel is produced according to the TBM procedure. The liquid steel is stirred in this case when gas is blown through the converter bottom. Thereby a better mixing of metal and slag is achieved. The Thyssen blowing-metallurgy (TBM)-process allows with that a better degree of purity. The ladle metallurgy [5] is in the same way important, especially for Ni-alloyed steels. It relieves the converter process and allows a very precise attitude of the targeted chemical composition as well as a setting of the sulfur content and phosphorus content onto extremely low values. That is favourable with regard to the degree of purity and results in a high safety against brittle fracture and an outstanding isotropy of the toughness and deformation properties. In nickel-alloyed high-strength steels (5% Ni and 9% Ni) the best combination of strength and toughness is reached with phosphorus contents around 0,010% and sulfur content below 0,003% [6,7], whereas a phosphorus content below 0,005% should exhibit no further advantage for the toughness.

Next to a balanced chemical composition of the steels as well as a modern steel works metallurgy, the use of modern rolling techniques and heat treatment techniques under consistent use of metallurgical mechanisms is vital from that. In the case of high-strength nickel-alloyed steels the production route consists of hot rolling and subsequent quenching and tempering.

To achieve a customer-oriented surface quality the descaling of the surface is important for nickel-alloyed high-strength steels, because scale has a strong influence on the plate´s surface properties. For this, a sophisticated descaling equipment is located after the reheating furnace for the slabs.

Fig. 5a, b show the process route in detail. The heat treatment is carried out in this case on effective furnaces and begins with heating up on temperatures above Ac3. After the heating a rapid cooling of the heavy plates with pressurized water occurs (quenching). For highly demands on the mechanical properties a double quenching before tempering can be adopted, whereas the second hardening occurs from the two-phase region $\alpha+\gamma$ (QLT-procedure). In future it is conceivable to simplify the process through direct quenching from the rolling-heat.

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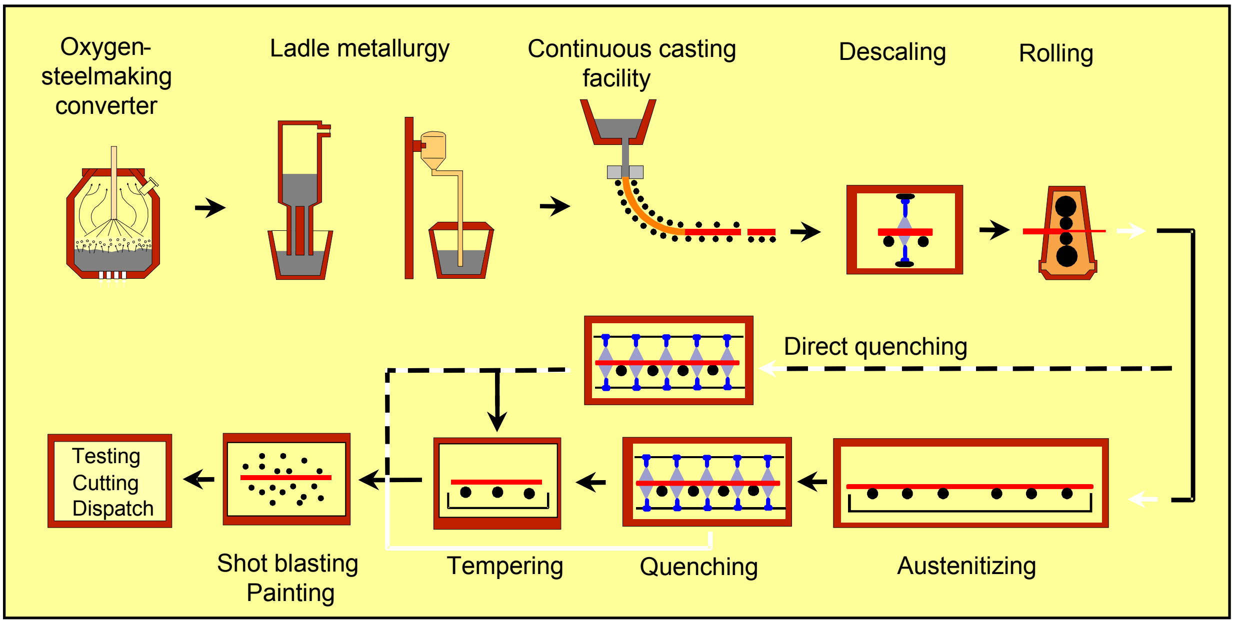

Fig. 5a: Production process of quenched and tempered nickel steel plates

Next to the chemical composition the tempering treatment after the quenching is the most important control factor for the mechanical properties. After the hardening procedure the microstructure of Ni-Steels consists of fine grained martensite with high Ni-content. Beyond that 9% Ni-steels show residual austenite after quenching [2,8,9]. The tempering procedure after hardening leads to intended changes in the microstructure. With an increasing tempering temperature the toughness increases. It can be concluded that the optimium tempering temperature for 9 % Ni-steels in the area of 600 °C. Resulting from that are the tempering temperatures specified in the above mentioned standards.

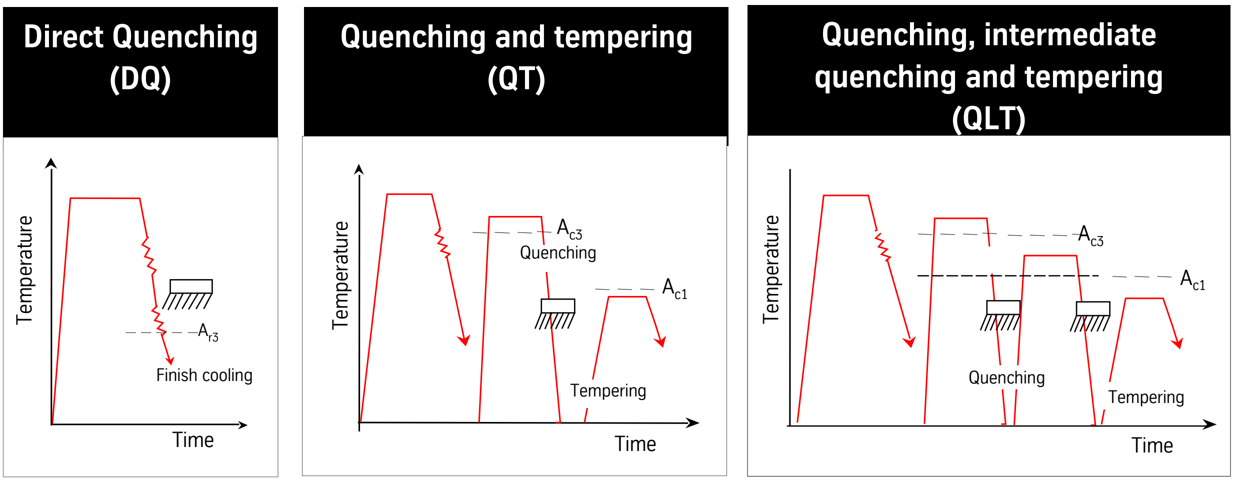

Fig. 5b: Heat treatment of 5% and 9% Ni-steels

Besides, ThyssenKrupp uses the special advantages of the heavy plate production via hot strip rolling during the production of water quenched steels up to thicknesses of 12 mm and widths up to 2000 mm. Through the advantages of that modern production route thickness tolerances can be achieved which in general at four-high mill plates with high additional costs can be kept.

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3. MECHANICAL PROPERTIES OF NICKEL-ALLOYED HIGH-STRENGTH STEELS

The mechanical properties of steels can be derived from the reactions of the atomic formation to forces acting from exterior.

- Strength and toughness properties

Fig. 6a and **Fig 6b** give an overview on measurements of strength and impact toughness properties of 5% and 9%-nickel steels produced by ThyssenKrupp Stahl AG with reference to the constraints given by the relevant standards. The influence of the plate thickness on yield strength, tensile strength and impact toughness is illustrated.

Typical chemical composition 5% Ni-steel					
C: 0,08 %	Si: 0,25 %	Mn: 0,65 %	S: 0,001 %	P: 0,008 %	Ni: 5,0 %

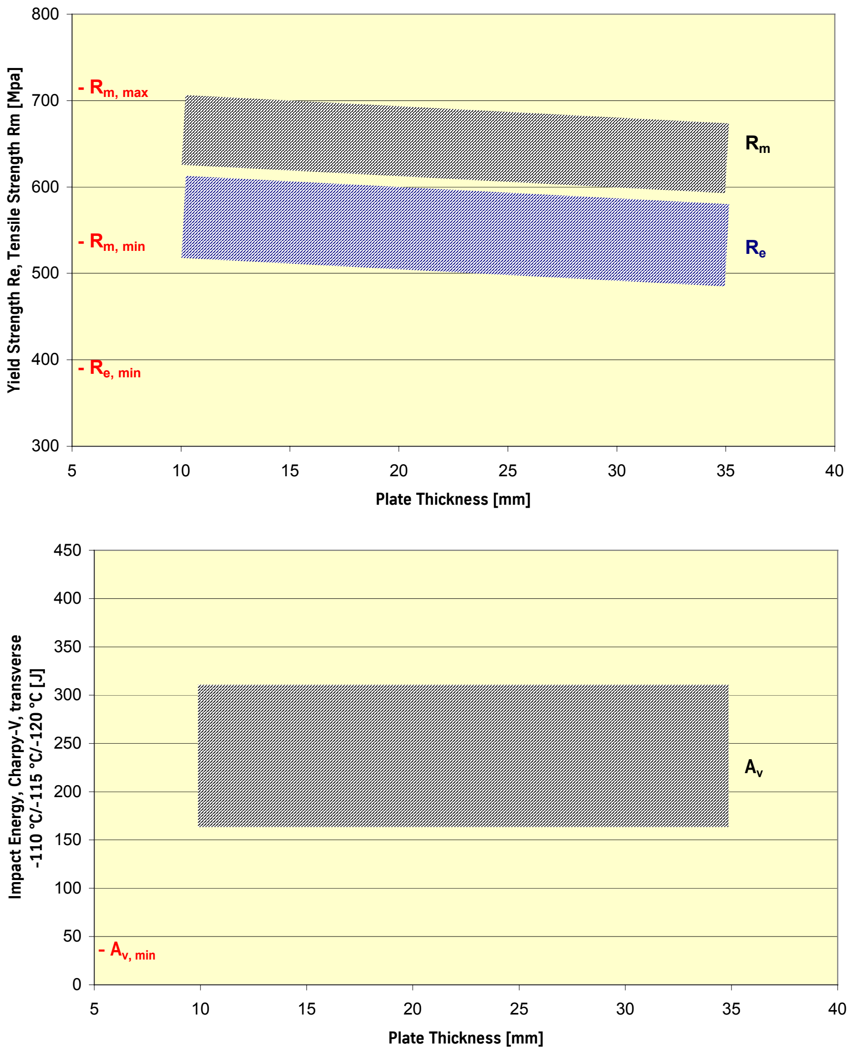
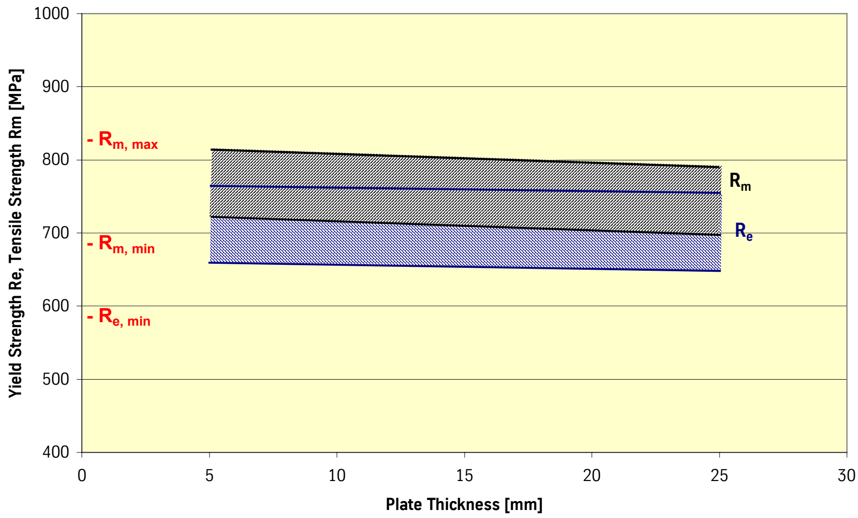


Fig. 6a: Mechanical properties of 5% Ni-steel (X 12 Ni 5 acc. EN 10028-4)

It is obvious that for 5% Ni-steels (grade X12Ni5 according to DIN EN 10028-4) the required minimum values are reliably reached. Values for yield strength, tensile strength and impact toughness do mainly not correlate with plate thickness in the interval under investigation. Especially toughness properties derived from impact testing with values > 200 Joule (with specified test temperatures between –110 °C and –120 °C, dependant on plate thickness) are on very high levels (Fig. 6a).

Typical chemical composition 9%Ni-steel					
C: 0,07 %	Si: 0,25 %	Mn: 0,40 %	S: 0,001 %	P: 0,007 %	Ni: 9,0 %



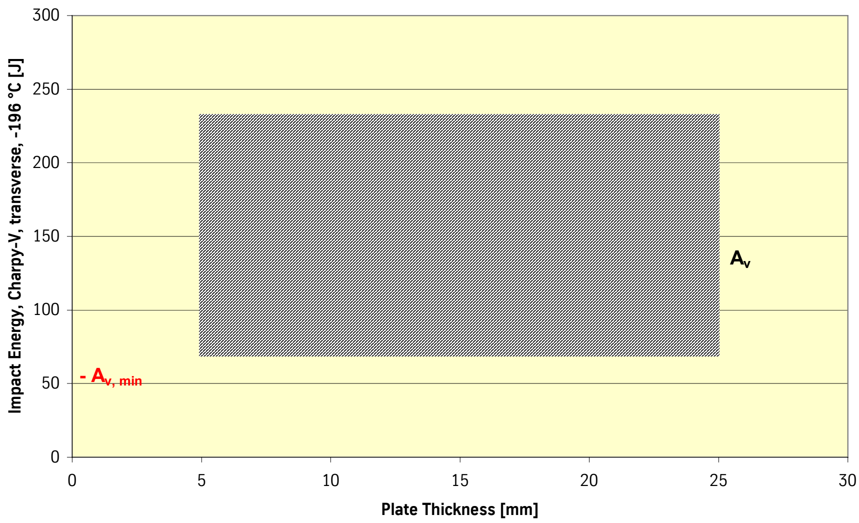


Fig. 6b: Mechanical properties of 9% Ni-steel (X 8 Ni 9 acc. EN 10028-4 or ASTM A 553 Type 1)

As expected in the case of 9% nickel-steel the level of strength is significantly higher compared to 5% nickel-steel. Simultaneous measurements of impact toughness after quenching and tempering show values from above 100 Joule up to round about 200 Joule even at the specified lower test temperature of –196 °C. There must be mentioned a positive influence of a double hardening procedure before tempering (QQT) on toughness properties. Already for a long time it is known that the increasing effect on the toughness of the QQT-procedure is especially great, if the second hardening occurs from the two-phase region $\alpha+\gamma$ (QLT-procedure) (see Fig. 5b) [2, 10]. However, this procedure is not in accordance with today´s delivery specifications as shown in Fig. 3.

Additionally, the lateral expansion of impact test specimen of 9% Ni-steel is often a required characteristic value in the case of deliveries in accordance with ASTM and ASME standards. Due to the high levels of toughness in the area from above 100 Joule values for lateral expansion are significantly over 0.5 mm.

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- Resistance against brittle fracture

For safe constructions of vessels using 5% and 9% nickel steels fundamental knowledge on brittle fracture behavior of these steels is of importance. In this context is has to be differed between the materials resistance against initial crack formation and it´s ability to stop crack propagation (crack arrest) [2]. The material´s resistance against initial crack formation prevents uncontrolled formation and growth of existing cracks. The ability to stop crack propagation is the material´s potential to stop the growth of instable propagation of cracks. The process of crack initiation can for example be investigated in a three-point bending test of a notched specimen that has been fatigue-precracked. In this test a notched specimen with a fatigue initiated crack is bended until material failure. Result of this test is the specification of a temperature above which brittle fracture (failure at low tensile loads) does not occur.

Because of occuring critical loads the ability to stop crack propagation is a rigorous criterion for steel selection. Results from drop weight tests with Pellini specimen exist for Ni-alloyed structural steels. The NDT-temperature can be characterized as the lowest temperature that allows to adjust crack propagation in the base material. In **Fig. 7** an overview on the characteristic critical temperatures for the material´s resistance against initial crack formation and the ability to stop crack propagation for 5% and 9% Ni-steels is given. In addition results from fracture mechanical tests to determine critical crack tip opening displacement values (CTOD) in accordance with BS 5762 are depicted for 9% Ni-steel. Thus it appears that critical crack tip opening displacement values of 0,3 mm to 0,5 mm occur even at temperatures of –170 °C. It is to mention that these values are δ_m-values, i.e. failure appears after stable crack propagation when the maximum load is reached.

Steel grade	Ni-content, %	typ. Yield Strength, MPa	Plate thickness, mm	Crack-start-temperature, °C									NDT-temperature, °C											CTOD, mm (-165°C)					
				-120	-140	-160	-180	-120	-140	-160	-180	-200	-80	-100	-120	-140	-160	-180	-120	-140	-160	-180	-200	0,1	0,2	0,3	0,4	0,5	0,6
X12Ni5	4,75-5,25	550	20-28																										
X8Ni9	8,50-10,00	720	25-28								< -195											< -195							
X7Ni9																													
ASTM A553, Typ I	8,50-9,50																												

Fig. 7: Overview on characteristic temperatures for brittle fracture behavior

- Forming behaviour

The processing of Ni-alloyed Steels to bottom plates and spherical segments, etc. is performed by cold forming or by hot forming. For these steels the same forming procedures as used for general structural steels are applied. Cold forming leads to strain hardening with increasing yield strength but decreasing toughness properties. The strain hardening induced by cold forming can in part be reduced by a stress relieving annealing procedure. Resulting detrimental effects on material properties from long term annealing are not expected [2].

- Welding

Welding is the joining technology which is of major importance for high-strength nickel-alloyed steels. Under observation of general technical rules (EN 1011), both 5% and 9% nickel-alloyed steels have very good weldability and are welded with Shielded Metal Arc Welding (SMAW) with covered electrodes and with Submerged Arc Welding (SAW). Gas Metal Arc Welding (GMAW) has been used occasionally at least on components in the workshop [11,12]. Austenitic or nickel based consumables are used to guarantee weld metal ductility and to reduce possibilities for hydrogen induced cracking. A detailed overview on the types of welding filler materials for 5% and 9%-Ni-steels is given in [2,11,12]. Unless the constructions are heavily restrained there is no need for pre-heating or post heat treatment when welding 5-9% nickel steels [11,12]. The interpass temperature should be kept below 150ºC. The peak hardness in HAZ will reach 250-320 HV10 at normal heat input between 1-3 KJ/mm.

SAW is a productivity welding method and is used for all the circumferential welds. SMAW is used manually for all vertical weldings of the shell plates. The requirements for toughness of the welded joints are extremely high to prevent initiation of a brittle fracture. To give an insight in the toughness of welded joints, **Fig. 8** shows the fracture toughness of a welded joint, welded by SAW. Here CTOD-values according to BS 5762 at temperatures of –170 °C of more than 0,25 mm are measured, which is in the same magnitude as for the base material (see Fig. 7).

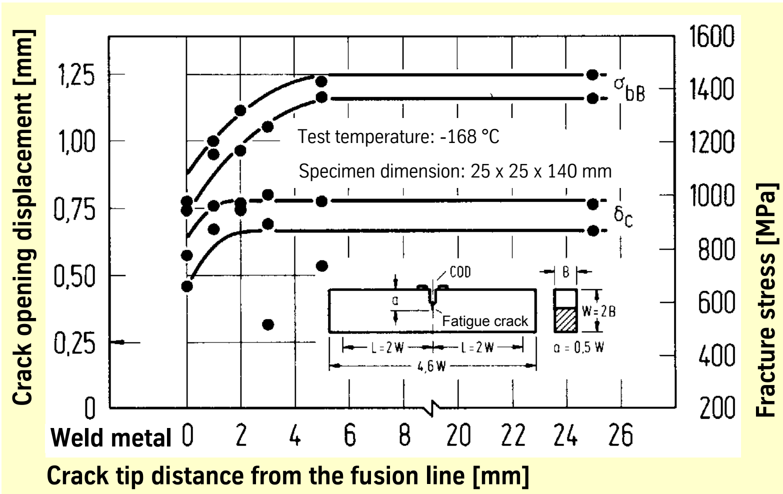

Fig. 8: Fracture behavior of a submerged arc weld joint of low temperature steel X 8 Ni 9 (Three-point bending test based on BS 5762)

4. DELIVERIES OF NICKEL-ALLOYED STEELS BY THYSSENKRUPP

ThyssenKrupp is a supplier of nickel-alloyed high-strength steels for more than three decades. In recent years a huge amount of heavy plates made from 9% Ni-steel has been delivered for several major projects in the LNG sector. In the context of the currently booming exploitation of natural gas resources and the accompanying need for storage and transportation facilities growing demand for 9% Ni-steels is perceived since the year 2004. ThyssenKrupp Stahl AG is a certified and accredited supplier for worldwide shipments of 5% and 9% Ni-steels for the fabrication of vessels. ThyssenKrupp Stahl AG is certified by renowned third party inspection agencies like

- Germanischer Lloyd
- Lloyd´s Register
- DNV
- CNSCPV

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The production of heavy plates is based on a fully developed Quality Management System (QMS) with specified supervision of the product in all stages of the plate fabrication including the acceptance procedure.

At present ThyssenKrupp Stahl AG is under production with 9% Ni-steels for the supply of several projects on LNG storage to be realized in 2006 to 2010. Recently ThyssenKrupp Stahl AG has delivered ca. 3.500 tons in 9% Ni-steel for a LNG storage facility for Marathon Oil company on Bioko Island in Equatorial Guinea. The plant is designed to produce 3.4 million metric tons of LNG per year and will start up in late 2007. The LNG tankage consist of two tanks with a total capacity of 272.000 cubic meters. The plate thickness varies from 5 to 25 mm. The LNG would be supplied primarily to a receiving terminal in Lake Charles, Louisiana, where it would be regasified and delivered into the gulf coast natural gas pipeline grid. **Fig. 9** gives an impression of an early stage of the building activities for the LNG-tanks at Bioko Island. Other current supplies of 9% Nickel-steels are provided for construction of LNG storage tanks on Sakhalin Island/Russia, in Texas/USA and in South Hook/UK.

Fig. 9: Construction of flat bottom tank (capacity 132.000 m^3), Bioko Island/Equatorial Guinea

5. FUTURE ASPECTS

9% Ni-steels exhibit an application-oriented property profile. To improve the properties in the future various studies are carried out to investigate the effect of an addition of Mo and the microalloying with Nb [7, 13, 14]. Here it was found, that through the addition of small amounts of Mo a slight increase in strength and toughness can be observed [7,15]. The first results from microalloying with Nb indicate, that Nb is especially useful for the improvement of the toughness in the HAZ.

To create new steel grades for low temperature applications the advantageous effect of thermomechanical rolling is currently examined at ThyssenKrupp Stahl AG. By deployment of thermomechanical controlled rolling in combination with accelerated cooling for steels with an appropriate Ni-content a remarkable strength-toughness relation is achieved. Brittle fracture behaviour and the suitability for cold and hot forming as well as welding of those steels are still to be investigated.

6. SUMMARY

High-strength structural steels with a Ni-content of 5 and 9 % are today´s materials of first choice for transport and storage of liquefied gases. Heavy plates of these steels correspond to the highest demands on strength, toughness and resistance against brittle fracture. This is due to modern procedures with melting, rolling and heat treatment. ThyssenKrupp exhibit a long-standing experience with the production of these steels on a high quality level. A huge amount of 9%-Ni-steels have been supplied during the last three decades for numerous large projects.

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