Permanent effect of a cryogenic spill on fracture properties of structural steels

2015 IOP Conf. Ser.: Mater. Sci. Eng. 102 012004

(http://iopscience.iop.org/1757-899X/102/1/012004)

ICMC 2015 IOP Publishing
IOP Conf. Series: Materials Science and Engineering **102** (2015) 012004 doi:10.1088/1757-899X/102/1/012004

Permanent effect of a cryogenic spill on fracture properties of structural steels

H Keseler[1], I Westermann[1], S Y Kandukuri[2], J O Nøkleby[2], B Holmedal[1]

[1] Norwegian University of Science and Technology, Department of materials science and engineering, Alfred Getz vei 2b, N-7491 Trondheim, Norway
[2] DNV GL, Veritasveien 1, N-1363 Høvik, Norway

E-mail: ida.westermann@ntnu.no

Abstract. Fracture analysis of a standard construction steel platform deck, which had been exposed to a liquid nitrogen spill, showed that the brittle fracture started at a flaw in the weld as a consequence of low-temperature embrittlement and thermal stresses experienced by the material. In the present study, the permanent effect of a cryogenic spill on the fracture properties of carbon steels has been investigated. Charpy V-notch impact testing was carried out at 0 °C using specimens, from the platform deck material. The average impact energy appeared to be below requirements only for transverse specimens. No pre-existing damage was found when examining the fracture surfaces and cross sections in the scanning electron microscope. Specimens of the platform deck material and a DOMEX S355 MCD carbon steel were tensile tested immersed in liquid nitrogen. Both steels showed a considerable increase in yield- and fracture strength and a large increase in the Lüders strain compared to the room temperature behavior. A cryogenic spill was simulated by applying a constant tensile force to the specimens for 10 min, at -196 C. Subsequent tensile tests at room temperature showed no significant influence on the stress-strain curve of the specimens. A small amount of microcracks were found after holding a DOMEX S355 MCD specimen at a constant force below the yield point. In a platform deck material tensile tested to fracture in liquid nitrogen, cracks associated with elongated MnS inclusions were found through the whole test region. These cracks probably formed as a result of the inclusions having a higher thermal contraction rate than the steel, causing decohesion at the inclusion-matrix interface on cooling. Simultaneous deformation may have caused formation of cracks. Both the microcracks and sulphide related damage may give permanently reduced impact energy after a cryogenic exposure.

1. Introduction

Liquid nitrogen is a widely used cryogenic liquid, which has a boiling point of approximately -196 °C. Cryogenic liquids are commonly used for various cooling purposes in the industry. Storage of large quantities of gas can also be done more effectively by condensing the gas into a liquid, as this will give a large volume reduction, e.g. the volume of liquefied natural gas will reduce the volume by a factor 600 compared to the gas volume [1-3].

Cryogenic liquids need to be kept at very low temperatures, hence, their storage and transportation set specific demands for the materials used in the storage tanks. A common way of storing cryogenic liquids is in insulated metal tanks, where the inner walls are made from aluminum or austenitic stainless steel. These are materials which retain their ductility at low temperatures. Carbon steels, on the other hand, are known to experience a ductile to brittle transition when reaching a critical low temperature, normally around -50 °C. In offshore applications, it is therefore important to keep cryogenic gases out of contact with the surrounding ship or platform structure, which is usually constructed from carbon steel. Exposure of the carbon steel structure to a cryogenic liquid, may lead to embrittlement and possibly also structural failure [3].

Because it is well known that carbon steels become brittle at low temperatures, this material is normally not used for such applications. For this reason little research has been done regarding the permanent consequence of exposing carbon steel to low temperatures or, as the case during a cryogenic spill, low temperatures combined with tensile stresses. Only two previous studies have been found, which concern the low-temperature behavior of carbon steel. The earliest of these studies was done in 1957 by Owen et al. [4]. They carried out tensile tests on a carbon steel at -196 °C using various cross-head speeds. Their results showed that the fracture always occurred after gross yielding of the specimen. When the cross-head speed was increased, the fracture stress increased with the yield stress. The observation of the strain patterns in pre-polished specimens showed that the fracture always was located within the Lüders band, and also that sub-critical microcracks were formed within the Lüders band prior to fracture. Another study concerning the low-temperature tensile properties of carbon steel was made by Goodenow and Bucher [5] in 1969. They confirmed the results seen by Owen et al., that tensile fracture of carbon steel at temperatures down to -196 °C occurred after the yield point had been reached. They defined a plastic instability transition temperature, TPI, as the temperature below which inhomogeneous plastic deformation would continue after the specimen had yielded. At this temperature the lower yield point stress was equal to the tensile stress and necking would occur as a result of different temperature dependencies of the yield- and tensile stress. In other words, decreasing the temperature made the initiation of yielding increasingly difficult and reduced the materials capacity for general work hardening increasing the Lüders plateau.

In 2011 the risk management and classification company DNV received a request concerning an incident where a large amount of liquid nitrogen had been spilled on a platform deck constructed from carbon steel plates of DNV grade NV E36. The combination of low-temperature embrittlement and thermal stresses experienced by the material during the cryogenic exposure had resulted in failure of the platform deck. After such incidents, the standard procedure is to replace only the visibly failed regions of the material, after thorough visual inspection and NDT, as no other permanent damage is known to result from such an exposure. Nevertheless, a larger region of the exposed material was cut from the platform for further examination. Charpy V-notch impact tests of the exposed area showed lower values than expected, whereas metallurgical examinations and tensile tests did not show any anomalies compared to non-exposed material. The reason for the failure was found to be a flaw in a weld, which had initiated an unstable crack growth.

In the present work, investigations have been done with the purpose of finding out if any permanent changes will occur in the fracture properties of carbon steel as a consequence of a cryogenic spill. Remaining material from the exposed platform deck has been subjected to fracture analysis in addition to Charpy V-notch impact testing to see if any permanent damage or deterioration of the fracture properties could be found and to investigate the possible mechanisms behind such damage. In addition the conditions during a cryogenic spill were simulated by tensile testing carbon steels in liquid nitrogen. Tensile stresses of various magnitudes were applied to simulate the thermal stresses arising from the temperature gradients during a cryogenic spill. The material was subsequently examined to see if any permanent damage had resulted from this treatment.

2. Material and experimental procedures

2.1. Material

The carbon steel used in the first part of the experimental work was cut from the platform deck, which had been exposed to a liquid nitrogen spill. The material was a hot-rolled steel of DNV grade NV E36 with plate thickness 12 mm. For the second part a 5 mm hot-rolled carbon steel plate of grade

DOMEX S355 MCD, with a similar strength as the platform material, was investigated in addition to the NV E36. The composition of the two materials is listed in Table 1.

Table 1 Chemical composition of the carbon steel grades given in mass % of the alloying elements. The exact composition is given for the DOMEX S355 MCD, whereas the composition of the NV E36 is defined from the specification.

	C	Si	Mn	P	S	Cr	Mo	Ni	Cu	Al	Nb	V	Ti
NVE36	0.20	0.10-0.55	1.70	0.030	0.030	0.20	0.08	0.40	0.35	min 0.02	0.02-0.05	0.05-0.10	0.007-0.05
S355	0.069	0.01	0.62	0.009	0.003	0.03	0.00	0.03	0.01	0.046	0.023	0.00	0.00

Figure 1 shows an overview of the original damaged platform material that was received by DNV in 2011. The arrows indicate the extension of the secondary cracks, which were assumed to have propagated from brittle areas and arrested when reaching more ductile material. The two plates that were used in the present study are outlined with dashed lines. These plates were further divided into smaller sections as indicated with dotted lines and numbered 1 to 5. The platform material was painted, and the paint had cracked in certain areas. This was assumed to be caused by differences in the thermal contraction between the paint and the underlying material during the liquid nitrogen exposure. The areas where the paint cracking was observed were expected to have been cooled to lower temperatures. Areas indicating cryogenic exposure will further on be referred to as exposed areas, whereas those with no paint cracking will be referred to as non-exposed.

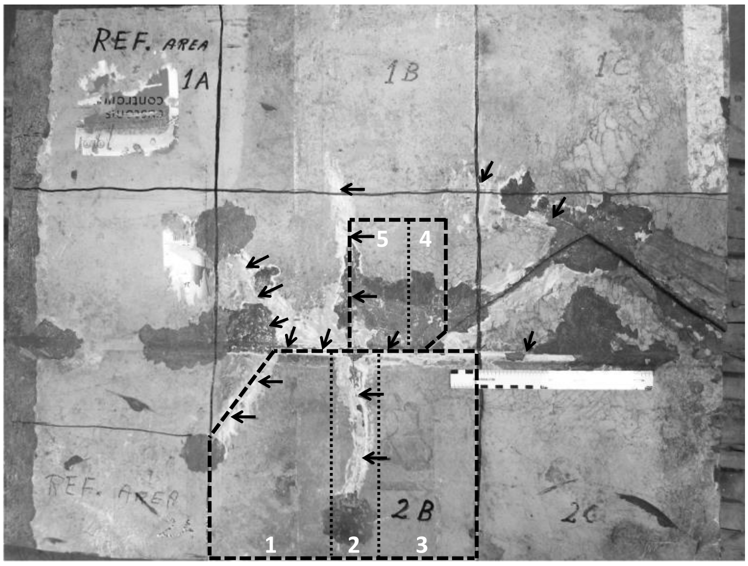


Figure 1. An overview of the platform material received by DNV. The two pieces used in this study is highlighted with dashed lines. Further subdivision is shown with dotted lines and the pieces are marked with numbers 1-5. The arrows indicate the extension of the crack formation.

2.2. *Examination of the platform material by Charpy V-notch impact testing*

Charpy V-notch impact testing was carried out using a Zwick/Roell RKP 450 apparatus with a theoretical impact velocity of 5.235 m/s, total pendulum mass of 32.85 kg and work capacity of 450 J. The specimens were cooled to 0 °C in an ethanol bath before testing.

Standard Charpy-V notch specimens were prepared as close to the plate surface as possible. The specimens were made with a square cross section of 10 mm × 10 mm, length of 55 mm and a 2 mm deep V-notch with angle 45° and 0.25 mm root radius, located at mid-length. 46 specimens aligned in the transverse direction were made from plate section 1, cf. Figure 1. From section 3 of the plate, 39 longitudinal Charpy specimens were made. Each of the sections contained both exposed and non-exposed areas.

2.3. *Simulation of a cryogenic spill by tensile testing in liquid nitrogen*

For the low temperature tests, a tensile test apparatus of the type MTS 880 was applied, with a tensile speed of 1 mm/min. An isolated plastic container was provided around the specimen holders to contain the liquid nitrogen during the immersed tests. No extensometer could be used in the cryogenic set-up. Therefore, the specimen strain was calculated as the difference in displacement taking into account the machine stiffness.

Small tensile specimens with a gauge diameter and length of Ø3 mm and 13 mm, respectively, were made from the DOMEX S355 MCD steel parallel to the rolling direction, and a few from section 2 of the NV E36 platform material (6 specimens). The liquid nitrogen was filled into the isolated container after the specimen was firmly tightened to the manual grips in the test rig. A holding time of 10-15 min was necessary to ensure that the specimen and the equipment had reached -196 °C.

Tensile curves at -196 °C were obtained as a reference for both the materials. To simulate tensile stresses from a cryogenic spill, samples were then held at different constant tensile force levels for 10 min at -196 °C. For the DOMEX S355 MCD three or four parallel samples were held at 1000 N, 4000 N and 6500 N. For the NV E36 material only two parallel samples were held at 5000 N, due to the low number of available samples. After 10 min the force was released, the nitrogen was removed, and the specimens were left in air at room temperature.

Subsequently all the prestressed specimens were further tensile tested to fracture at room temperature to see if the previous cryogenic treatment had affected the tensile properties. Reference tensile curves at room temperature were also conducted for comparison. These were tested in an MTS 810 test machine equipped with an extensometer allowing measuring the strains up to approximately 16%. The remaining strain to fracture was calculated by extrapolation of strain versus displacement data.

2.4. Metallographic examination

Two small samples were cut from each of the sections 2 and 4, from a non-exposed and an exposed area, respectively. A Leica Axiovert 25 optical microscope was used to compare the microstructure in the exposed and non-exposed material both parallel and perpendicular to a reference weld. This investigation was also necessary to determine the rolling direction of the investigated material.

Specimen preparation was carried out by standard metallographic preparation, i.e. mechanical grinding on SiC-paper with decreasing roughness followed by mechanical polishing with diamond spray of 3 μm and 1 μm. Finally, the specimens were etched for 10 sec in a 2 % Nital solution.

2.5. SEM examinations

The fractographic examination of both Charpy impact tested specimens and the tensile tests were carried out in a Zeiss Supra 55 VP LVFE SEM using the secondary electron signal. The SEM was operated at 10-20 kV and a working distance of 11-17 mm.

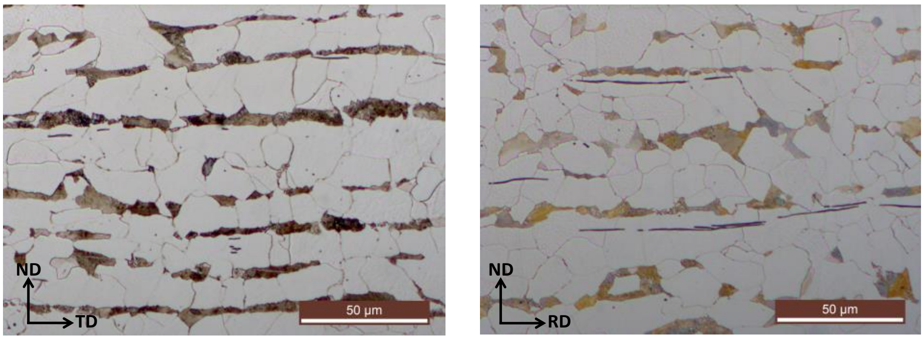
The Charpy impact specimens were investigated edge on, but also in a cross section perpendicular to the fracture surface, as the specimens were cut and polished in the length direction. The tensile specimens were similarly investigated edge on as well as in the cross sectional length direction. The latter was done for both specimens that only had been strained at cryogenic temperatures as well as specimens strained to fracture.

For the edge on investigations, the specimens were cleaned in an ultrasonic bath with acetone, and for the mid-section investigations, the samples were prepared similarly as for the metallographic examination.

3. Results and discussion

3.1. Charpy V-notch impact test of the platform material

The light optical images in Figure 2 show the microstructure of the platform material. In (a) the microstructure from a non-exposed area in a plane perpendicular to the rolling direction, and (b) for a cryogenic exposed material in a plane parallel to the rolling direction. In both cases the microstructure consists of ferrite and elongated pearlite and contains long manganese sulphide inclusions elongated in the rolling direction; cf. Figure 2(b). No obvious differences between the two microstructures could be observed of the exposed and non-exposed areas of the plate.



(a) (b)

Figure 2. The microstructure of (a) material from a non-exposed area in a plane perpendicular to the rolling direction, and (b) from cryogenic exposed material in a plane parallel to the rolling direction.

Figure 3 shows the numbering and position of the transverse Charpy specimens taken from section 1 of the plate in Figure 1. The Charpy impact energy for the given specimen is marked in the white boxes. The average value of the measured impact energies was 38.68 J. However, large variations are observed within the plate, with a maximum value of 76.49 J and a minimum of 24.47 J.

Similarly, Figure 4 shows the position and numbering of the longitudinal Charpy specimens taken from section 3, where the Charpy impact energy is marked for each specimen. In the longitudinal direction, the Charpy impact values are in general higher with an average value of 102.83 J, but also here large variations are found in the energy, ranging between 52.20 J and 144.71 J

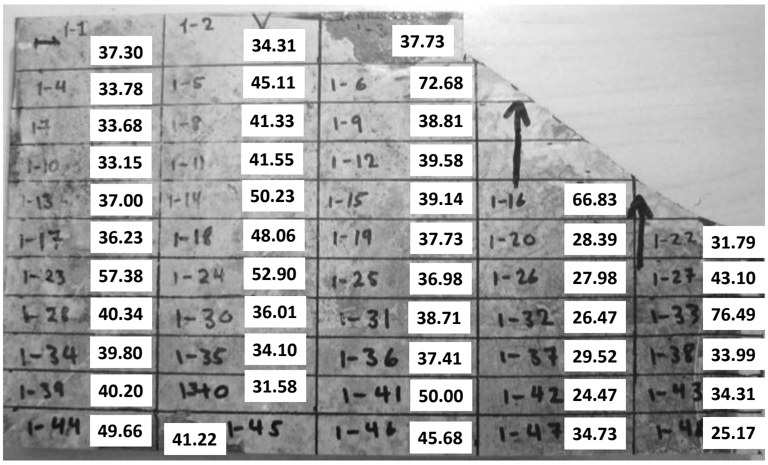


Figure 3. The sectioning of plate 1 into transverse Charpy specimens and their corresponding impact toughness values, given in Joules [J], at 0 °C.

The specified Charpy V-notch impact energy of NV E36 steel at -40 °C is 34 J in the longitudinal direction and 24 J in the transverse direction [6]. These values are given as minimum values and the real impact values of the material are expected to be significantly higher. In this work the impact test were performed at 0 °C. As a rule of thumb, the impact energy increases by 1 Joule for 1 °C increase in temperature. At 0 °C this leads to required impact energies of approximately 74 J and 64 J in the longitudinal and transverse direction, respectively. According to the standard [7] the minimum requirement should be met by the average of three test pieces. It can be accepted if one individual value is below the specified value, provided that it is not less than 70 % of this value.

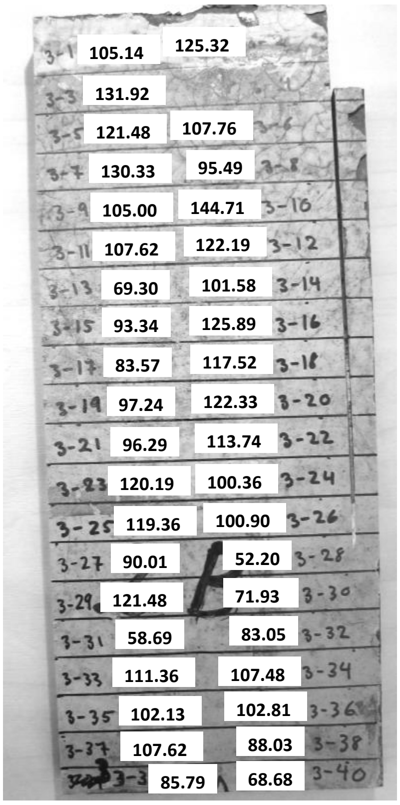


Figure 4. The sectioning of plate 3 into longitudinal Charpy specimens and their corresponding impact toughness values, given in Joules [J], at 0 °C.

The longitudinal Charpy specimens are well within the requirement, whereas the transverse specimens are far too low in impact energy. A rather large variation in impact energy is observed. The reason for this might be random variations caused by microstructural inhomogeneities through the material. However, it could also be a consequence of stress relief occurring in the region close to the main crack.

3.2. Simulation of a cryogenic spill by tensile testing in liquid nitrogen

In Figure 5 the reference curves obtained at -196 °C for the NV E36 and the DOMEX S355 MCD are presented. The noise is a side effect from the test machine used and should be neglected. For the DOMEX S355 MCD a clear upper yield point is observed. Then the stress drops and slowly decreases until fracture at around a strain of 15 %. The NV E36 show a less clear upper yield point. The stress-strain curve then enters a stage where the stress is almost constant, before fracture occurs at strains around 26 %. Compared to the reference curves obtained at room temperature shown in Figure 6 the yield strength significantly increases with decreasing temperature. However, the appearance of the stress-strain curves is quite different. The long horizontal or decreasing region after the upper yield point is believed to be caused by propagation of Lüders bands across the length of the specimen. The large Lüders strains seen at -196 °C can be explained by the low work hardening rate at this temperature. This is in accordance with the observations by Goodenow and Bucher [5], who observed a reduced work hardening rate and increased upper yield strength with decreasing temperature. Instead of a ductile-to-brittle transition, they observed a so-called plastic instability transition when the temperature decreased below a certain point. At this plastic instability transition temperature, the tensile stress is equal to the lower yield stress and necking occurs within the Lüders strain. In the case of the NV E36 steel tested here, the work hardening rate was probably just large enough for the Lüders band to spread over the length of the test region.

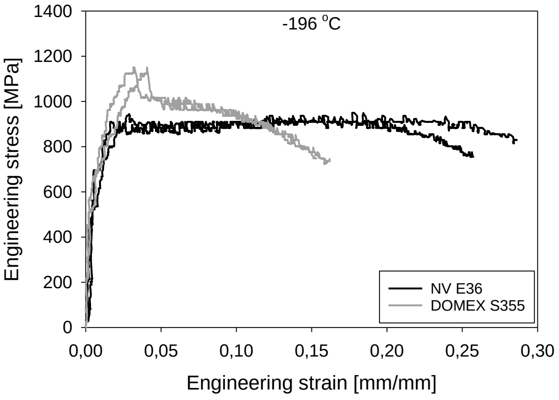
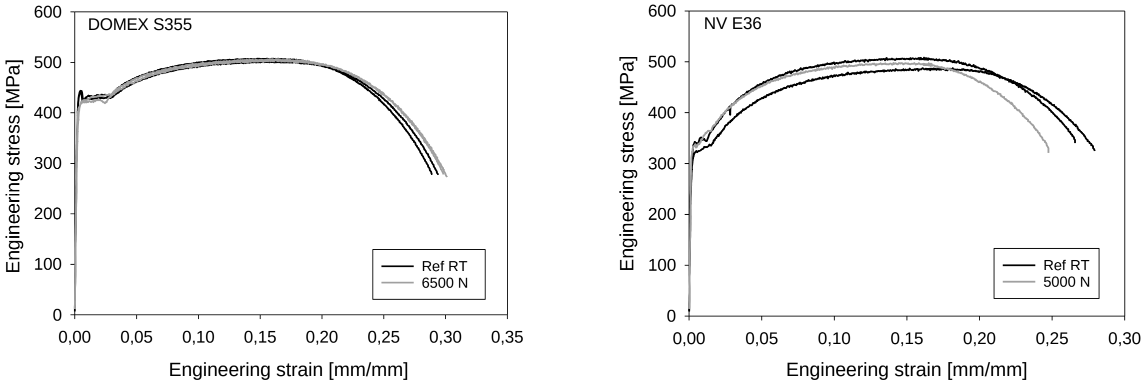


Figure 5. The engineering stress-strain reference curves for the two materials tested at -196 °C.

Figure 6 shows the room temperature engineering stress-curves of reference material that has not been exposed to liquid nitrogen, along with material that has been held at a force below the yield point in liquid nitrogen for 10 min. Only the stress-strain curve for the material held at the maximum constant force (6500 N) is shown here for the DOMEX S355 MCD.



(a) (b)

Figure 6. Engineering stress-strain curves obtained at room temperature for non-exposed reference material and material strained at a force below the yield point for 10 min in liquid nitrogen. (a) DOMEX S355 MCD and (b) NV E36.

No particular difference is observed between the stress-strain curves, except that the upper yield point gradually disappeared for the DOMEX S355 MCD material when the tensile force applied under cryogenic conditions was increased. The fracture surface of the pre-strained material also appeared ductile after tensile testing at room temperature.

SEM investigations of the longitudinal cross section of a DOMEX S355 MCD sample that only had been exposed to liquid nitrogen at a force of 6500 N revealed a few microcracks as shown in Figure 7. Some of the cracks were located at grain boundaries, but mostly they appeared in the grain interior. For comparison the longitudinal cross section of an untreated specimen was investigated, and no microcracks were found in this material.

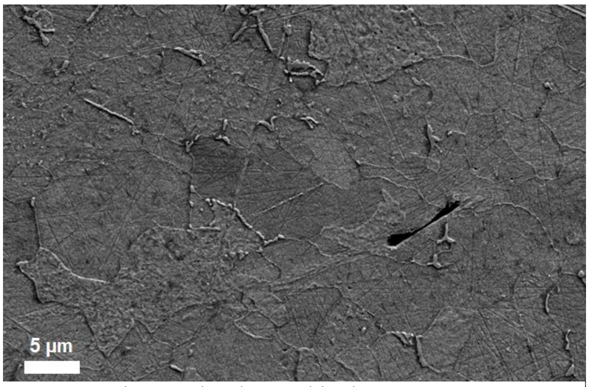
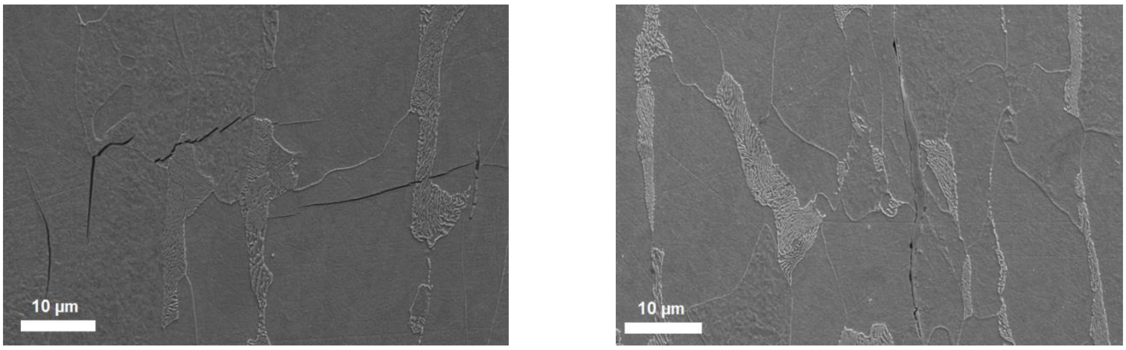


Figure 7. Microcracks observed in the DOMEX S355 subjected to 6500 N under cryogenic conditions.

Figure 8 shows two types of microcracks that were found in the NV E36 material tested at -196 °C. Figure 8(a) shows a type of microcrack which was only found at small distances from the fracture surface. These cracks were mainly oriented parallel to fracture surface. Another type of microcrack found in the longitudinal cross section is shown in Figure 8(b). These cracks were always directed along the rolling direction and are associated with elongated manganese sulphides. Such cracks were observed to occure through the entire test region of the tensile specimen, and the extent of these cracks could be through several ferrite grain boundaries. The reason for the formation of the sulphide related cracks is believed to be a combination of the low temperature and the high stresses in the material. Brooksbank and Andrews [8] showed that MnS inclusions have a linear thermal expansion coefficient that is higher than for steel (18×10^{-6} °C^{-1} vs. 12×10^{-6} °C^{-1}). This means that when the material is cooled, the MnS inclusions will contract at a higher rate than the steel. The result can be decohesion, and possibly also void formation at the inclusion-matrix interface.



(a) (b)

Figure 8. Two types of microcracks observed in the RD-ND plane in the NV E36. (a) microcracks near the fracture surface and (b) cracks associated with MnS.

The latter type of cracks may also explain the observed direction dependency observed in the Charpy impact tests, where the poorest impact energy is observed when the notch is located parallel to the rolling direction as sketched in Figure 9. Cracks aligned with the direction of the notch will have a detrimental effect on the properties.

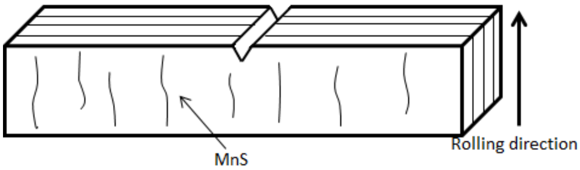


Figure 9. Sketch of the transverse Charpy specimens showing the alignment of the microstructure in the rolling direction.

4. Conclusion

Material from the platform deck that had been exposed to a liquid nitrogen spill was subjected to Charpy V-notch impact testing. The impact energy was below the minimum requirement for the transverse specimens. The impact energy of the longitudinal specimens was above the requirement. This is believed to be either due to differences in the temperature and stress history of the regions the specimens were taken from, or due to an orientation dependent damage mechanism. No evidence of pre-existing damage was found in the Charpy specimens. However, from examination of specimens tensile tested in liquid nitrogen, two possible mechanisms for reduced impact energy after a cryogenic spill were found.

The first mechanism is believed to be the formation of microcracks before fracture, occurring when carbon steel is cooled to low temperatures and simultaneously subjected to high thermal tensile stresses. A small number of microcracks were seen in a specimen of DOMEX S355 MCD carbon steel after holding 10 min at a force below the yield point in liquid nitrogen. The presence of microcracks is expected to reduce the impact energy in both the transverse and longitudinal orientations.

The second possible mechanism which was found is the formation of damage associated with elongated manganese sulphide inclusions. It is believed that cracks were formed due to manganese sulphides having a higher thermal contraction rate than the steel. When the material was cooled this caused decohesion and possibly also void formation at the inclusion-matrix interface. Due to the orientation of the manganese sulphides in the rolling direction, the reduction in impact energy is expected to be larger for in the transverse direction than the longitudinal direction in accordance with what is measured.

The tensile behaviour of the platform material and a DOMEX S355 MCD carbon steel at -196 °C showed largely increased yield- and fracture strength compared to at room temperature. A large increase in the Lüders strain occurs for both the materials due to a low work hardening rate at this temperature. Both steels showed plastic instability, as the fracture occurred within the Lüders strain region. The DOMEX S355 MCD steel showed the most pronounced plastic instability, as necking started directly after the upper yield point. For the platform material, necking would first occur when the Lüders band had spread through approximately the whole test region of the tensile specimen.

A cryogenic spill was simulated by cooling specimens of the two materials to a temperature of -196 °C in liquid nitrogen, and applying a constant force below the yield point for a period of 10 min. This showed no significant effect on the subsequent room temperature tensile behavior, indicating that a cryogenic spill will not permanently affect the tensile behavior of these steels.

From the results of this work, it is believed that a cryogenic spill can permanently damage the fracture properties of carbon steel. Therefore, the standard repair procedure after such incidents, which is to only remove the visibly damaged material, may be insufficient. Microcracks or sulphide related damage may be present in apparently undamaged material and can reduce the impact energy in these regions.

References

[1] Tomsic J 2000 “Dictionary of materials and testing” 2nd ed. (Warrendale, PA: Society of Automotive Eng.)
[2] Mokhatab S, Mak J Y, Valappil J V, Wood D A 2013 *Handbook of Liquefied Natural Gas* (Oxford: Gulf Professional Publishing)
[3] Kumas S, Kwon H T, Choi K H, Lim W, Cho J H, Tak K, Moon I 2011 *Appl. Energy* **88** 4264
[4] Owen W S, Averbach B L, Cohen M “Brittle fracture of mild steel in tension at -196C” 1957 Technical report: SSC-109 Prog Rpt. National Technical Information Service
[5] Gooden R H and Bucher J H 1969 *J. Fluids Eng.* **91** 603
[6] Det Norske Veritas 2011 “Rules for classification of ships/high speed, light craft and naval surface craft” (Part 2) (Høvik: Det Norske Veritas)
[7] Det Norske Veritas 2012 “Metallic materials – offshore standard” (Høvik: Det Norske Veritas)
[8] Brooksbank D and Andrews K W 1968 *J Iron Steel Inst* **206** 595