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THE EFFECT OF LOW LEVELS OF MOLYBDENUM IN HIGH STRENGTH LINEPIPE STEELS

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Abstract

Heavy plates for large-diameter linepipes are produced using low-carbon microalloyed steels by thermomechanical rolling. In combination with accelerated cooling, this processing strategy has made it possible to achieve yield strength levels of 690 MPa and above in combination with attractive technological properties. While the focus in the case of high strength grades above the 485 MPa yield strength level was initially on heavy plate with moderate wall thickness, improved low-temperature toughness and weldability at higher wall thicknesses have gained importance in recent years. This has made it necessary to adapt the steel composition and the processing parameters in order to maintain the balance of properties.

The microstructure that is obtained after accelerated cooling from the homogeneous austenite depends on the steel composition and the cooling conditions. Alloying additions that retard ferrite formation are used in order to obtain a predominantly bainitic microstructure. Molybdenum is well known to be especially effective in this respect and is, therefore, used frequently in high strength linepipe grades at a level of 0.2% or higher. However, this leads to an increase of the carbon equivalent which impairs weldability. In an experimental investigation that was carried out at Salzgitter Mannesmann Forschung GmbH, three laboratory heats were cast with a variation of the molybdenum content up to 0.2%. Coupons were rolled down to a wall thickness of 25 mm followed by accelerated cooling. The plates were characterized with regard to their microstructure, tensile properties and low-temperature toughness. In addition, welding trials were carried out in order to assess the toughness in the heat affected zone and the influence of the molybdenum content. It was found that an addition of 0.1% molybdenum led to a strength increase while excellent levels of low-temperature toughness were maintained in the base material and in the heat affected zone.

Introduction

High strength linepipe steels offer an economic advantage compared to lower strength grades as they allow a reduction in wall thickness of the pipe at the same operating pressure. This leads to savings with regard to raw materials, transportation and field welding. Conversely, they allow an increase of the operating pressure at the same wall thickness. Since the first application of X80 large-diameter pipes more than 25 years ago, the combination of mechanical properties required by customers has become increasingly complex, due to the strong worldwide interest to develop remote natural gas resources in hostile environments. These can include pipeline operation under arctic conditions or in areas with ground movement. High deformability and low-temperature toughness are therefore critical requirements in order to ensure pipeline safety. The optimization of the toughness has, therefore, been a strong focus of development.

Since the beginning of the 1980s, heavy plates, pipes and pipe bends of X80 with a minimum yield strength of 555 MPa have been developed and produced by Salzgitter Mannesmann Grobblech GmbH (SMGB) and EUROPIPE and have become daily business for both companies as long as the requirements are merely according to EN 10208-2 [1], API 5L [2] or equivalent. In recent years, however, the complexity of requirements for linepipe materials has increased steadily with regard to toughness and weldability. SMGB has reacted to these demands with continuous alloy and process development in cooperation with Salzgitter Mannesmann Forschung GmbH (SZMF) in order to offer economically feasible solutions and guarantee safe operation for these scenarios.

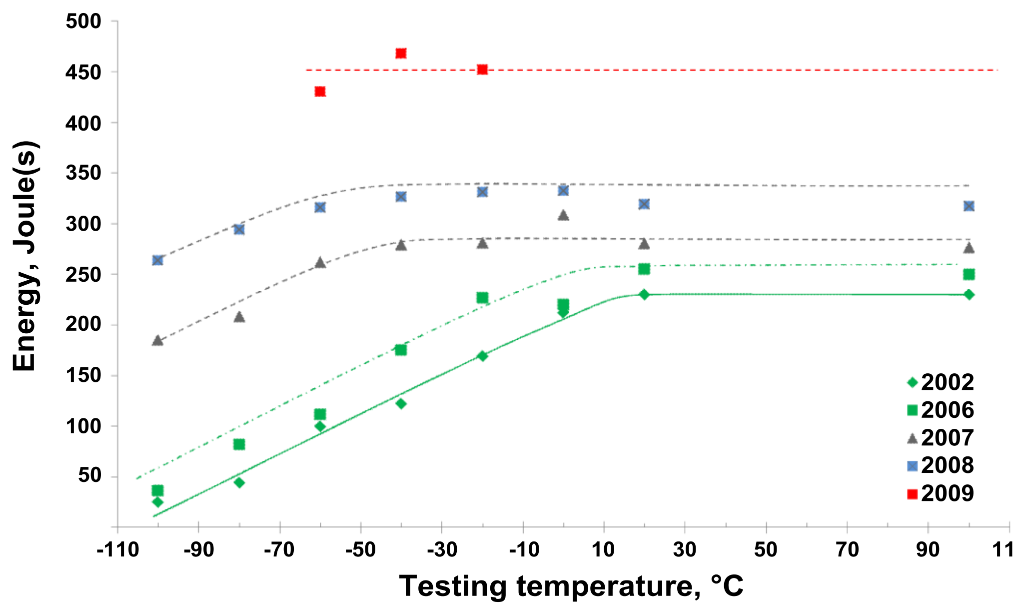


Figure 1. Development of Charpy properties and requirements for SMGB X80 plates since 2002 for a plate thickness between 25 and 30 mm.

The first X80 pipes were developed and produced according to specifications with a focus on elevated strength level with no specific requirements for low-temperature toughness in the base metal or the heat affected zone (HAZ). Since then, more and more emphasis has been placed on toughness [1-4]. Since 2002, SMGB has produced X80 plates above 25 mm wall thickness, which presented an additional challenge compared to the first X80 plates with lower wall thickness. The toughness development for X80 heavy plates since 2002 is illustrated in Figures 1 and 2. The requirements regarding minimum Charpy impact energy, as well as the shear area fraction in drop-weight-tear (DWT) tests, increased constantly. As shown in Figure 1, the upper shelf energy was raised from a level of 230-250 J at a testing temperature of 10 °C in 2002 to 2006 to 450 J at -60 °C in 2009. This went hand in hand with an improvement of the shear area in the DWT test, where the 85% shear area transition temperature was lowered from 0 °C down to -50 °C in 2009.

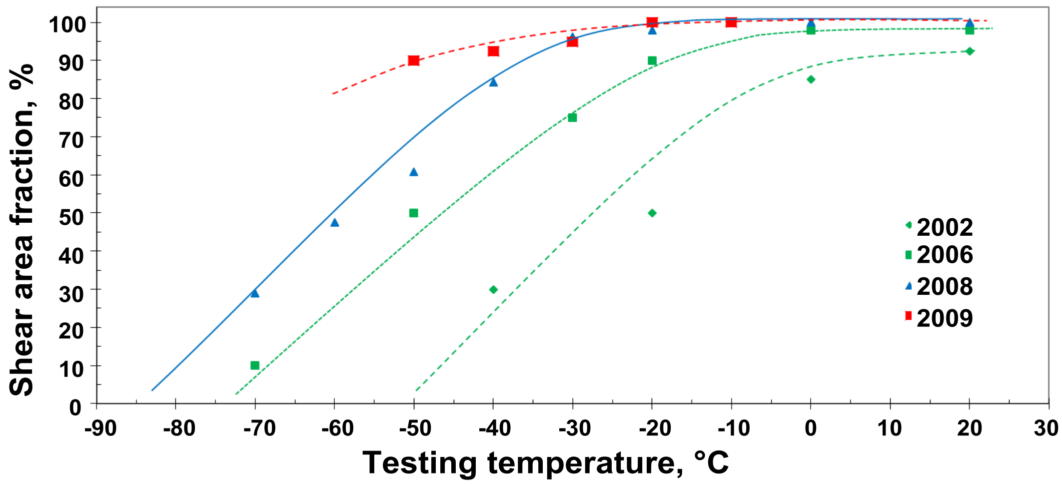


Figure 2. Development of shear area in the DWT-test for SMGB X80 plates since 2002 for a plate thickness between 25 and 30 mm.

Submerged-arc welding of large-diameter pipes requires a high heat input in order to achieve the welding speeds necessary for practical production. This leads to significant changes in the microstructure in the heat affected zone (HAZ) [5]. These include grain coarsening and the formation of carbon-rich constituents in a bainitic matrix in the vicinity of the fusion line. It has been demonstrated that the alloy design of the plate material in combination with the processing parameters during welding plays a key role for achieving a high level of HAZ toughness at low temperatures [6].

Continuous alloy and process development made it possible to achieve the X80 strength level and reduce the level of alloying elements at the same time. This is illustrated in Figure 3 which shows the reduction of the carbon equivalent range (CE_{IIW}) of X80 since 1990. The reduction of the CE_{IIW} improved the weldability while material costs were maintained in a reasonable range. Achieving the right balance of all material properties places tight restrictions on the alloy design and processing strategy at all stages of production.

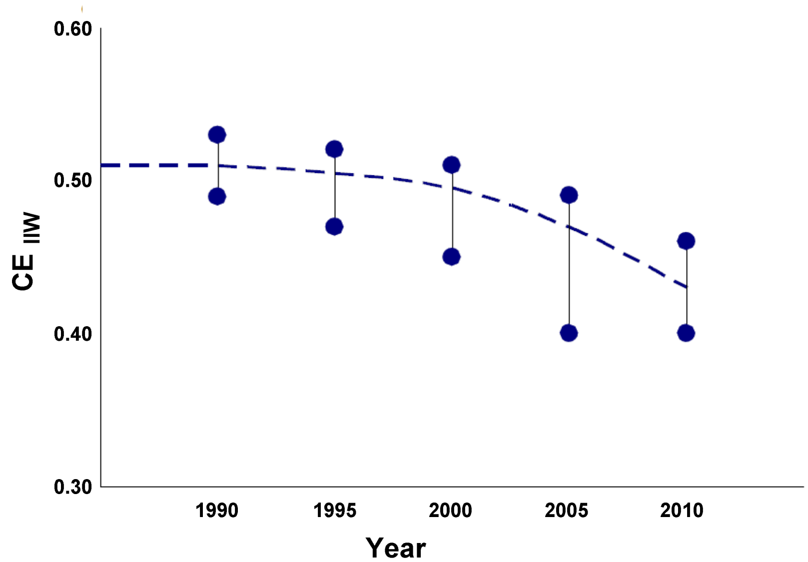


Figure 3. Development of the carbon equivalent CE_{IIW} of X80 since 1990.

Modern high strength heavy plates for large-diameter pipes are produced using low-alloy, low carbon steels which are microalloyed with niobium. They are generally produced by thermomechanical rolling (TMCP) followed by accelerated cooling. This processing route results in a microstructure that predominantly consists of bainite. The combination of high strength and high toughness in these steels is a result of the microstructure realized by TMCP and is strongly influenced by the alloy design and the processing conditions during heavy plate production.

In order to generate a predominantly bainitic microstructure, accelerated cooling has to begin above the temperature at which austenite transforms to ferrite, ie. above the Ar_3 temperature. This is a function of the steel composition and it has been shown that the addition of molybdenum lowers the Ar_3 temperature more effectively than the addition of the same level of copper, nickel or chromium [7]. Classically, molybdenum levels of 0.2% or above are used in high strength linepipe steels. This has a significant effect on alloying costs and on the weldability of high strength heavy plates compared to lower strength grades. However, it has also been shown that a combined addition of chromium and molybdenum is more effective in promoting bainite formation than an addition of only one of these elements [8]. It is also well known that molybdenum can lower the sensitivity to temper embrittlement of steels by reducing the enrichment of tramp elements at austenite grain boundaries. The aim of the present investigation was, therefore, to examine the effect of molybdenum additions of 0.1% and 0.2% in combination with 0.2% chromium on the mechanical properties and the weldability.

Production of Laboratory Heats and Rolling Trials

100 kg laboratory heats were produced by vacuum induction melting with a variation in the molybdenum content from 0 to 0.2%, as shown in Table I. The carbon equivalent (IIW) varied between 0.42 and 0.46. The ingots were sectioned into coupons and were rolled on a two-high rolling mill down to a wall thickness of 25 mm. Final rolling temperatures above the Ar_3 temperature were selected for all three compositions in order to ensure a predominantly bainitic microstructure after accelerated cooling, which was interrupted above the martensite start temperature at around 450 °C.

Table I. Composition of the Investigated Laboratory Heats (wt.%)

Steel	**C**	**Si**	**Mn**	**Cr**	**Mo**	**Others**	**CE_{IIW}**	**Pcm**
0 Mo	0.07	0.3	1.8	0.2	0.0	Nb, Ti	0.42	0.18
0.1 Mo	0.07	0.3	1.9	0.2	0.1	Nb, Ti	0.45	0.19
0.2 Mo	0.07	0.3	1.9	0.2	0.2	Nb, Ti	0.46	0.20

The reheating temperature was selected above the equilibrium dissolution temperature of Nb(C,N) precipitates based on thermodynamic calculations. Once these are dissolved, only Ti(N,C) particles can inhibit grain coarsening, because these precipitates are stable over the whole range of feasible reheating temperatures.

Reheating at excessively high temperatures leads to grain coarsening, which can have a detrimental effect on the toughness of the product, because the grain size of the final product increases as well [9]. On the other hand, it has been shown that increasing the reheating temperature leads to an increase in the strength of the heavy plate [10]. Finding the right balance between the dissolution of Nb(C,N) and austenite grain coarsening during reheating is, therefore, important in order to achieve the desired combination of mechanical properties in the final plate product.

Microstructure Characterization

Longitudinal sections of the plates were characterized by scanning electron microscopy (SEM) in combination with electron backscatter diffraction (EBSD), since light-optical microscopy offers only limited possibilities to characterize the microstructure in detail, because of the low magnification and resolution possible with this technique. It was found that a predominantly bainitic microstructure with small volume fractions of ferrite and carbon-rich constituents was achieved in all cases. SEM images of the samples taken close to the plate surface and at the mid-wall position are shown in Figure 4. Carbon rich constituents with a size below 3 µm were observed either along grain boundaries or between bainite sheaves. They varied in character from retained austenite to martensite and carbon-rich bainite. During the bainitic transformation, carbon is continuously redistributed to the austenite which leads to a significant enrichment in these regions which can reach levels that stabilize the austenite down to room temperature. The transformation product that is formed then depends on the local composition and the cooling rate.

EBSD-measurements were carried out close to the plate surface and at the mid-wall position. These make it possible to characterize the microstructure quantitatively in more detail, eg. with regard to the cell size, the local misorientation or the texture. The correlation of these properties with the alloy composition and processing parameters has been the focus of materials development at the SZMF [11,12]. Maps of the kernel average misorientation (KAM) of the investigated plates close to the surface and at the mid-wall position are shown in Figure 5, which illustrate orientation gradients between 0° and 3° within domains. These domains or cells are defined as areas with a minimum misorientation of 15° with respect to neighboring domains. Blue areas denote regions of lower misorientation, ie. lower local strength, and green or yellow areas are regions of higher local misorientation, ie. higher local strength. The average cell size was found to be below 2.6 µm in all three steels and did not vary significantly with the molybdenum content or the position through the wall thickness.

All three steels showed roughly similar distributions of the local misorientation close to the plate surface. However, the fraction of the areas with low misorientation increased significantly from the plate surface to the mid-wall position in the case of the steels with 0%Mo and 0.1%Mo, while the steel with 0.2%Mo showed the weakest increase of areas of low misorientation. The qualitative observation of the decrease of areas with low misorientation was confirmed by a quantitative analysis of the distributions of the kernel average misorientation for the three steels at the mid-wall position, as shown in Figure 6. These distributions typically have a positive skew. It was found that the position of the peak or mode of the distribution was shifted to higher values with increasing molybdenum content from 0.34° (0 Mo) to 0.44° (0.1 Mo) and 0.53° (0.2 Mo). The median values increased from 0.54° (0 Mo) to 0.59° (0.1 Mo) and 0.68° (0.2 Mo).

Since the rolling and cooling conditions were held constant within experimental limits in the trials, the observed variation of the local misorientation, depending on the position, can be attributed to the difference in the molybdenum content of the steels and is related to the inherent decrease of the cooling rate from the surface to the centre of the plate during accelerated cooling. Those regions with a lower misorientation originate from phase transformation at higher temperature, while regions of higher misorientation, on the other hand, were transformed at a lower temperature. This shows that the addition of molybdenum inhibits the transformation at higher temperatures effectively and improves the homogeneity of the microstructure over the wall thickness.

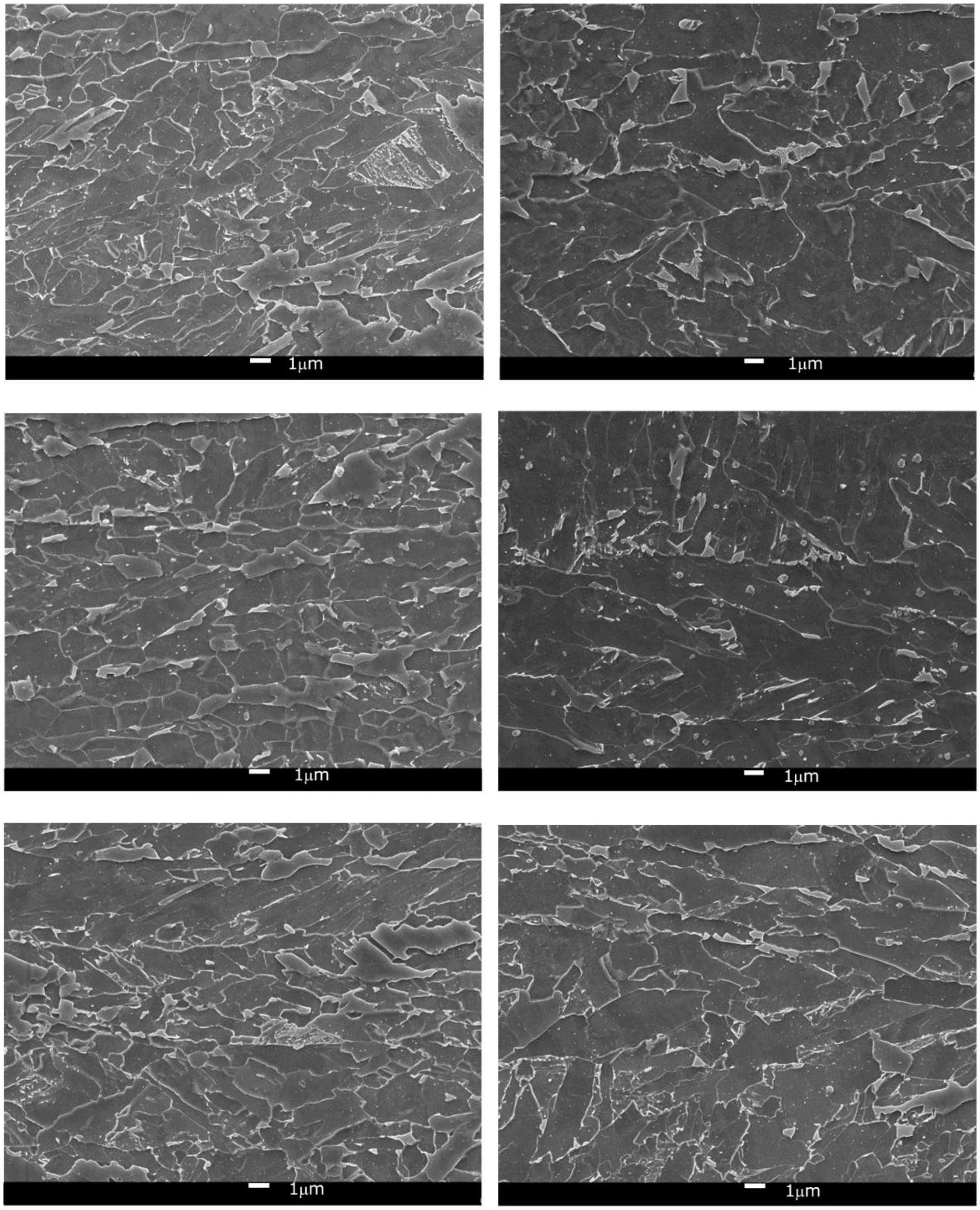


Figure 4. SEM-images of the microstructure of the laboratory-rolled plates close to the surface (left) and at the mid-wall position (right) of steel 0 Mo (top), 0.1 Mo (center) and 0.2 Mo (bottom).

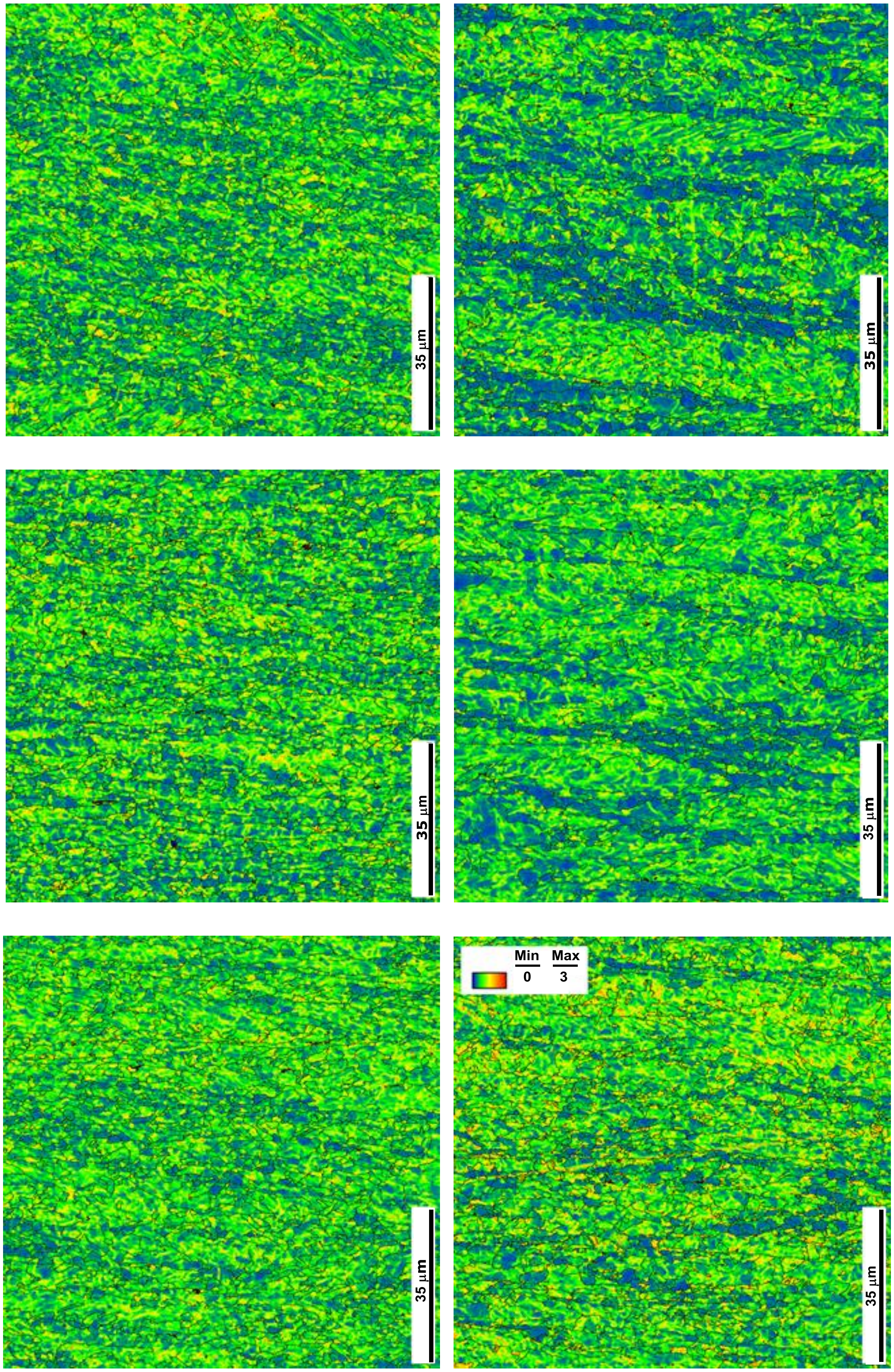


Figure 5. Kernel average misorientation between 0° and 3° of the laboratory-rolled plates close to the surface (left) and at the mid-wall position (right) of steel 0 Mo (top), 0.1 Mo (center) and 0.2 Mo (bottom).

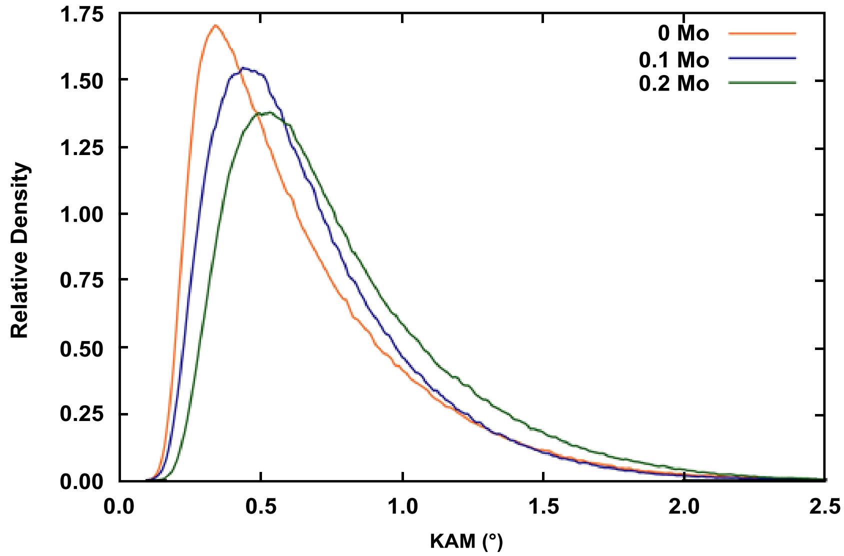


Figure 6. Distribution of the kernel average misorientation (KAM) of the laboratory-rolled plates at the mid-wall position.

Mechanical Properties

Materials testing consisted of tensile tests on round bar specimens, Charpy impact tests and pressed-notch (PN) Battelle drop-weight-tear tests at -20 °C in the transverse direction using specimens with the full wall thickness.

The transverse tensile results from the plates (see Figure 7) showed that the X80 requirements (SMYS 555 MPa, SMTS 625 MPa) in the transverse direction with regard to the yield strength and tensile strength were fulfilled by all three compositions. The yield strength increased continuously with increasing molybdenum content from 610 MPa to 676 MPa and the tensile strength increased from 672 MPa to 729 MPa. The increase of strength was concomitant with an increase of the yield to tensile ratio from 0.91 to 0.93.

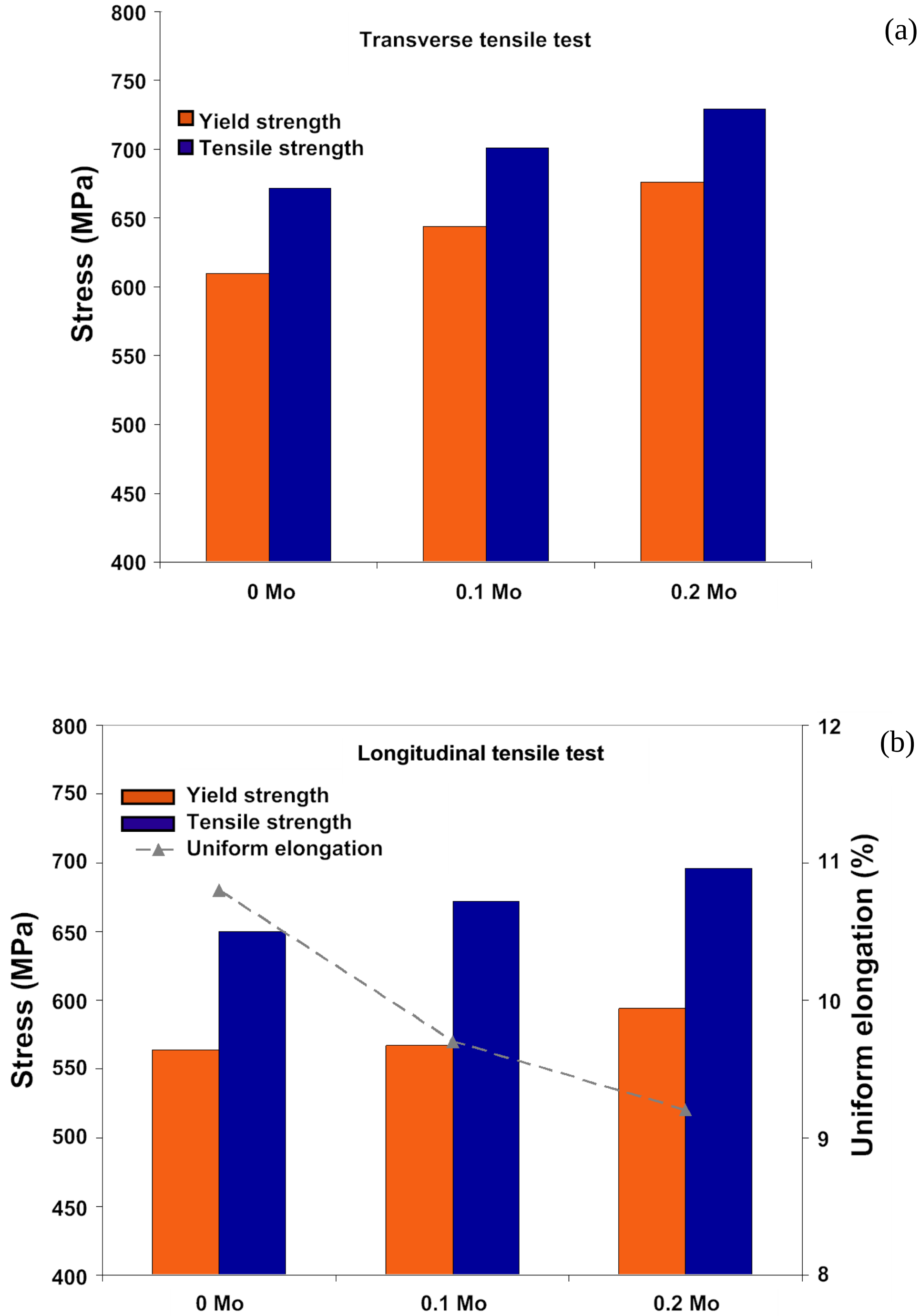


Figure 7. Results of tensile tests in transverse (a) and longitudinal direction (b).

In the longitudinal direction, the yield strength increased with increasing molybdenum content from 564 MPa to 594 MPa and the tensile strength increased from 650 MPa to 696 MPa, ie. the X80 specification minimum values were also fulfilled in the longitudinal direction. The yield to tensile ratio was between 0.87 and 0.84. The uniform elongation decreased with increasing molybdenum content from 10.8% to 9.2%.

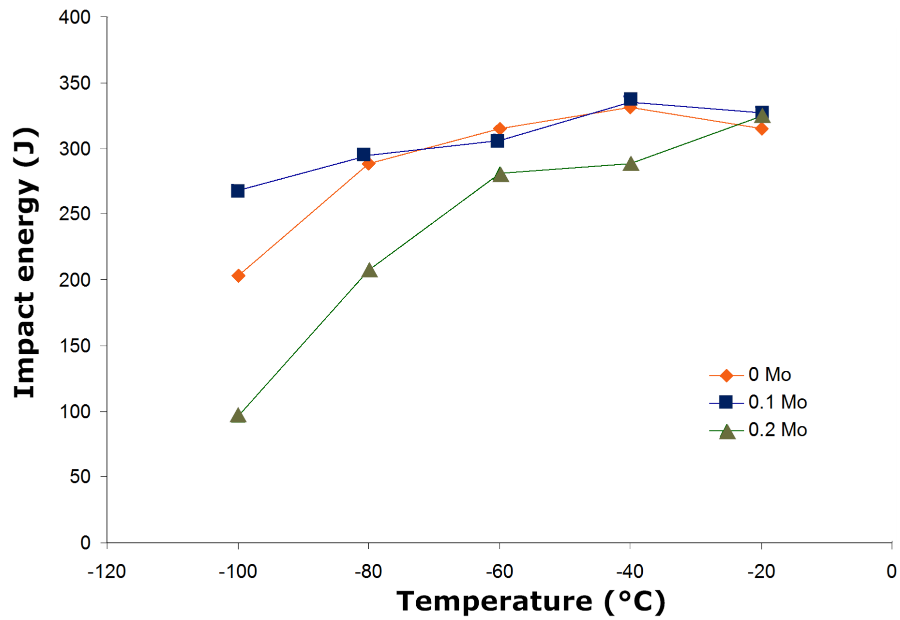


Figure 8. Average impact energy of samples in transverse direction.

Charpy impact tests were carried out in the transverse direction between -20 °C and -100 °C. The average impact energy is presented in Figure 8 as a function of the testing temperature. Down to -60 °C, an excellent level of impact energy, in the range from 250 J up to 350 J with little scatter of individual values, was observed. There was no significant difference in this range between the 0 Mo and 0.1 Mo steels with values around 300 J, while slightly lower values were found for the 0.2 Mo steel which showed a decrease of the impact energy below -60 °C. At -100 °C, the 0.1 Mo steel showed the highest average energy value with purely upper shelf behavior, whereas the 0 Mo and 0.2 Mo steels showed considerable scatter of individual values. While the impact energy at testing temperatures below -60 °C may not be relevant for a specification, the results indicate differences in the potential for low-temperature application. In this respect, the 0.1 Mo steel is clearly superior to the 0.2 Mo steel.

Drop-weight-tear tests (DWTT) were carried out at a testing temperature of -20 °C in the transverse direction using pressed-notch specimens with the full wall thickness. The average shear area and minimum-maximum range is shown in Figure 9. Typical acceptance criteria are an average value of ≥85% and a lowest single value of 75% shear area fraction. The results show that these criteria were not fulfilled in the case of the 0 Mo steel which only attained an average shear area of 84%. The 0.1 Mo and 0.2 Mo steels, on the other hand, fulfilled the criteria with average values of 90%.

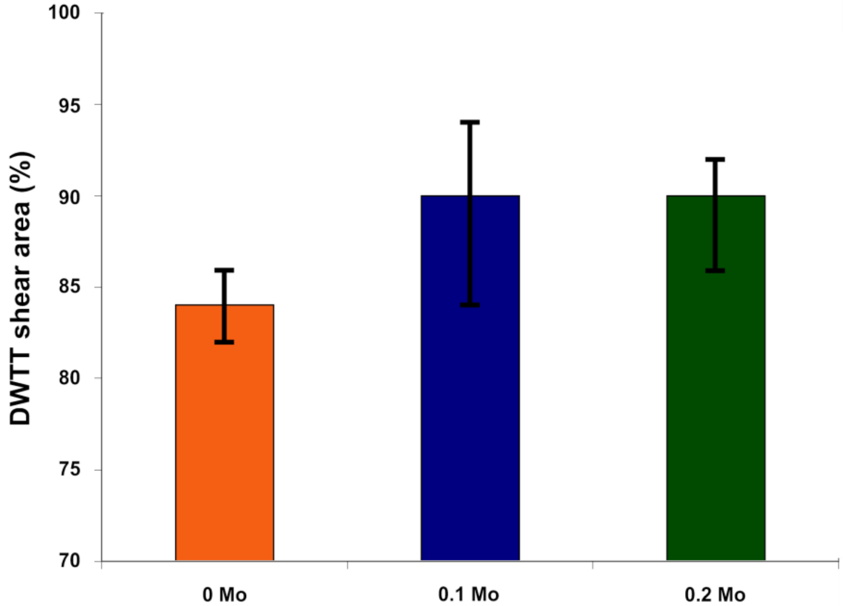
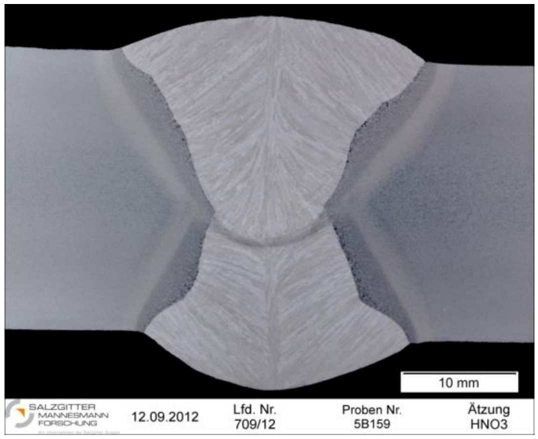


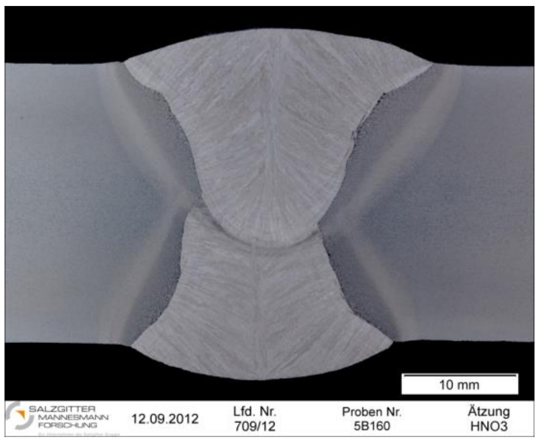
Figure 9. Average DWTT shear area and minimum-maximum range at -20 °C.

Submerged Arc Welding Trials

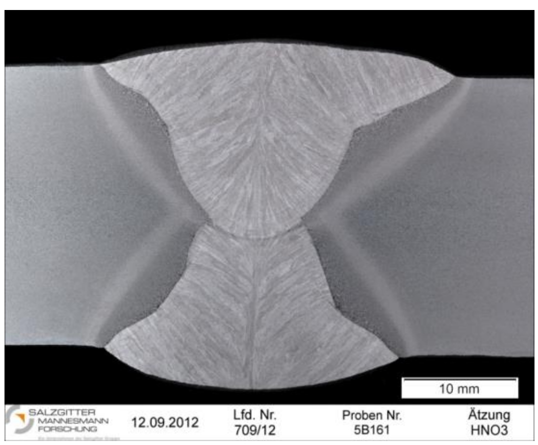
Double-layer submerged arc welding trials were carried out on the laboratory-rolled plates. The welding parameters were held constant and resulted in a heat input of 50-60 kJ/cm for the inner and outer weld seams. The same welding consumables were used in these trials for all welds. The welding conditions that were used are realistic for the production of large-diameter pipes with a 25 mm wall thickness. Macrographs of the welds are presented in Figure 10.



(a)



(b)



(c)

Figure 10. Macrographs of the laboratory welds produced using the steels 0 Mo (a), 0.1 Mo (b) and 0.2 Mo (c).

Charpy V-notch tests were carried out between 0 °C and -20 °C on six samples per testing temperature in the HAZ of the outer weld seam, 2 mm below the plate surface, in order to compare the HAZ toughness of the investigated materials. The notches of the Charpy specimens were positioned so that the tested cross section contained 50% weld metal and 50% HAZ (FL 50/50). At a testing temperature of 0 °C, the 0 Mo and 0.1 Mo steels showed similar average impact energies around 190 J, whereas the average for the 0.2 Mo steel was 130 J, see Figure 11. At a testing temperature of -10 °C, the average value of the 0.1 Mo steel (117 J) dropped below the level observed in the case of the 0 Mo steel (159 J), but was still slightly above the value for the 0.2 Mo steel (100 J). At -20 °C, all three steels showed similar average values of between 90 J and 100 J.

The three steels fulfilled typical requirements for toughness in the heat affected zone, eg. 56 J average and 45 J minimum, within the investigated temperature range. However, the results confirm that the HAZ toughness decreases with increasing molybdenum content. In the case of lower design temperatures, measures have to be taken to improve the toughness. Possible strategies have been outlined recently and could include a reduction in the silicon content or the carbon content [6]. The positive effect of a reduction of the silicon content has been noted previously and attributed to the reduced stability of retained austenite [13,14]. Since the 0.2 Mo steel showed the lowest toughness, a combination of both steps may be necessary in order to achieve a sufficient improvement. Both measures would, however, lead to a decrease of the strength level. This could be compensated for by an increase of the niobium content above 0.06% which has been found to improve the strength without impairing the HAZ properties significantly [15,16].

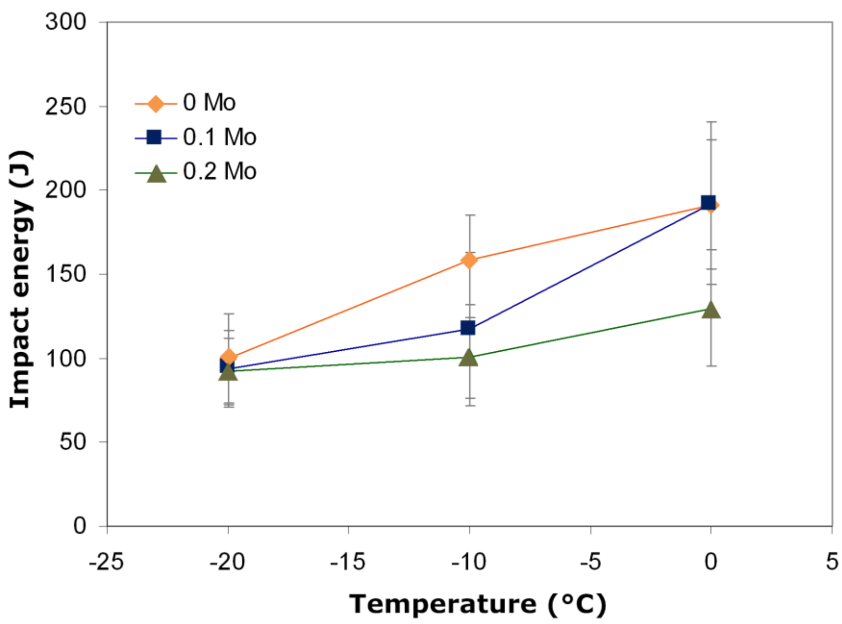


Figure 11. Average impact energy and standard deviation at the FL 50/50 position.

Conclusions

A laboratory trial was carried out with the aim to investigate the effect of the molybdenum content on the microstructure, mechanical properties and HAZ toughness of linepipe steels at the X80 strength level. Thermomechanical rolling down to a wall thickness of 25 mm in combination with accelerated cooling from above the Ar_3 temperature resulted in a predominantly bainitic microstructure. In EBSD investigations, the 0 Mo and 0.1 Mo steels showed a significant variation in the local misorientation from the plate surface to the mid-wall position, whereas only a minor variation was observed in the case of the 0.2 Mo steel, ie. the homogeneity of the microstructure was improved with increasing molybdenum content. The variation of the local misorientation is related to a decrease in the cooling rate from the surface to the mid-wall position. The extent of this effect is higher as the plate thickness increases.

The tensile tests showed that all three steels fulfilled X80 requirements, that both the yield strength and the tensile strength increased with increasing molybdenum content and that an addition of only 0.1% molybdenum has a strengthening effect in combination with 0.2% chromium. The Charpy tests showed that a higher level of impact energy at low temperatures can be reached if a molybdenum addition of 0.1% is used while all other alloying elements are held constant. A beneficial effect of a molybdenum addition was also found in DWT tests at -20 °C.

The effect of the molybdenum content on the HAZ toughness was investigated by submerged arc welding trials. The toughness level was sufficient for all three steels down to -20 °C. The lowest level of toughness in the HAZ was found for the 0.2 Mo steel, while the 0.1 Mo steel showed a higher toughness at 0 °C and -10 °C. It is possible that higher levels of toughness can be realized if the alloy design is improved, eg. by a reduction of the silicon or carbon content. The concomitant drop in strength could be compensated for by an addition of niobium above 0.06%.

References

1. EN10208-2: Steel Pipes for Pipelines for Combustible Fluids – Technical Delivery Conditions – Part 2: Pipes of Requirement Class B10208-2.

2. ANSI/API Specification 5L, 44th ed., 1 October, 2007.

3. G. Wilkowski et al, "Effect of Grade on Ductile Fracture Arrest Criteria for Gas Pipelines," *Proceedings of the Sixth International Pipeline Conference*, Calgary (2006), IPC2006-10350.

4. M. Erdelen-Peppler et al., "Investigations on the Applicability of Crack Arrest Predictions for High Strength Linepipe at Low Temperatures," *Proceedings of the 2nd International Conference on Super-High Strength Steels*, Peschiera del Garda, Italy (2010).

5. A.D. Batte, P.J. Boothby and A.B. Rothwell, "Understanding the Weldability of Niobium-bearing HSLA Steel," *Proceedings of the International Symposium Niobium* (2001), Orlando, 931.

6. C. Stallybrass et al, “Influence of Alloying Elements on the Toughness in the HAZ of DSAW-Welded Large-diameter Linepipes,” *Proceedings of the 9th International Pipeline Conference,* Calgary (2012), IPC2012-90118.

7. C. Ouchi, T. Sampei and I. Kozasu, “The Effect of Hot Rolling Condition and Chemical Composition on the Onset Temperature of γ-α Transformation after Hot Rolling,” *Transactions of the Iron and Steel Instititue of Japan*, 22 (1982), 214.

8. A.M. Llopis, “ Effect of Alloying Elements in Steels on the Kinetics of the Austenite to Bainite Transformation” (DOE Technical Report, DOI 10.2172/7283325, California University, 1975).

9. M. Militzer and E.B. Hawbolt, “Austenite Grain Growth in Microalloyed Low Carbon Steels,” *Corrosion,* 37 (5) (1981), 247-256.

10. C. Stallybrass et al, “Development of High Strength Heavy Plate Optimised for Low Temperature Toughness for Linepipe Applications,” *Proceedings of the Pipeline Technology Conference,* Ostend (2009), Ostend 2009-003.

11. C. Stallybrass et al., “High Strength Heavy Plate Optimised for Application in Remote Areas and Low-temperature Service,” *Proceedings of the 8th International Pipeline Conference*, Calgary (2010), IPC2010-31227.

12. J. Konrad et al., “Characterisation of the Microstructure of X80 Heavy Plate for Pipeline Applications using the EBSD Method,” *Proceedings of the 3rd International Conference on Thermomechanical Processing of Steels*, Padua (2008).

13. R. Taillard et al., “Effect of Silicon on CGHAZ Toughness and Microstructure of Microalloyed Steels,” *Metallurgical and Materials Transactions A*, 26A (1995), 447.

14. M. Gräf and K. Niederhoff, “Properties of HAZ in Two-pass Submerged Arc Welded Large-diameter Pipe, *Proceedings of the 3rd International Pipeline Technology Conference*, Brugge, May (2000), 553.

15. K. Hulka and F. Heisterkamp, “Physical Metallurgy, Properties and Weldability of Pipeline Steels of Various Niobium Contents,” *Proceedings of International Conference on Technology and Applications of HSLA Steels*, Philadelphia, (1983), 915-924.

16. B. Bersch and K. Kaup, “Effect of Niobium on the Welding Behavior of Thermo-mechanically Rolled Steels,” *3R international*, 10 (1983), 484-492.