Development of NbTiB micro-alloyed HSLA steels for high-strength heavy plate

H. Meuser Mannesmannröhren Mülheim GmbH, Mülheim/Ruhr, Germany
F. Grimpe Mannesmannröhren Mülheim GmbH, Mülheim/Ruhr, Germany
S. Meimeth Mannesmannröhren Mülheim GmbH, Mülheim/Ruhr, Germany
C. J. Heckmann Salzgitter Mannesmann Forschung GmbH, Duisburg, Germany
C. Träger Salzgitter Mannesmann Forschung GmbH, Duisburg, Germany

Microalloying for New Steel Processes and Applications Int. Symposium
September 7-9, 2005, San Sebastian, Spain

Development of NbTiB micro-alloyed HSLA steels for high-strength heavy plate

H. Meuser[1, a], F. Grimpe[1, b], S. Meimeth[1, c], C. J. Heckmann [2, d], C. Träger [2, e]

[1] Mannesmannröhren Mülheim, Wiesenstr. 36, 45473 Mülheim/Ruhr, Germany

[2] Salzgitter Mannesmann Forschung, Ehinger Str. 200, 47259 Duisburg, Germany

[a]heike.meuser@mannesmann-mrm.de, [b]fabian.grimpe@mannesmann-mrm.de,
[c]stefan.meimeth@mannesmann-mrm.de, [d]c.heckmann@du.szmf.de, [e]c.traeger@du.szmf.de

Keywords: Heavy plate, Boron, High strength low alloy, Thermomechanical treatment, Bainitic microstructures.

Abstract

This paper deals with the development of low carbon NbTiB micro-alloyed high strength low alloy steel for heavy plates with high wall thickness. In the production of heavy plate it is remarkably difficult to achieve a combination of high strength and good low-temperature toughness. Bainitic microstructures have shown the capability to attain such requirements. To achieve a bainitic microstructure even for heavy wall products the formation of bainite can be promoted and supported by the use of small amounts of boron as a micro-alloying element. This industrial research project is based on the addition of small amounts of boron to promote the desired bainitic structure. Mill rolling trials were carried out to determine the optimum process parameters. The results of experimental mill rolling trials on 35 mm plates will be presented in this paper.

Introduction

Due to its segregation behaviour to the austenite grain boundaries boron is an efficient promoter of a bainitic microstructure by retarding the austenite to ferrite transformation. But only boron in free solution is known to be effective. To keep boron in free solution it is of great importance to avoid the precipitation of boron-carbonitrides. This can be avoided by the addition of the micro-alloying element titanium which neutralises the precipitation forming elements such as carbon and nitrogen. The additional use of niobium further promotes the formation of a bainitic microstructure [1, 2, 3]. This kind of micro-alloying concept can only be effective in combination with an optimised thermomechanical rolling process followed by accelerated cooling.

Design and processing of NbTiB steel

Bainitic microstructures have shown the capability to achieve a combination of high strength and good low-temperature toughness. The desired microstructure can be promoted by the addition of small amounts of boron (< 40 ppm), where boron segregates to the austenite grain boundaries. Boron also has a high affinity to carbon and nitrogen, but it can only act as a promoter of a bainitic microstructure when it is in free solution. The undesired formation of coarse $Fe_{23}(CB)_6$ precipitates can be prevented by the reduction of the carbon level below 0.06 %. By adding titanium the formation of boron-nitrides can be prevented. The level of titanium is controlled as a function of the nitrogen level in order to ensure a stoichiometric Ti/N ratio. Niobium inhibits the nucleation and growth of ferrite and helps in the homogenous distribution of boron to austenite grain boundaries. Therefore, the amount of solute carbon not combined with niobium is reduced [1-5].

The chemical composition which is presented in this paper contains amongst the above mentioned elements all other alloying components that ensure the safe production of a high strength line pipe grade such as API X80. The basic alloying concept is given in **Table 1**.

Table 1: Basic chemical composition (weight-%)

C	Si	Mn	Nb	Ti	Others	CE_{IIW}	PCM
0.04	0.30	1.90	0.05	0.02	Mo, B	0.40	0.18

Since boron has been shown to shift the ferrite nose in time-temperature-transformation diagrams (**Fig. 1**), one should expect little change in the microstructure over a wide cooling range [3].

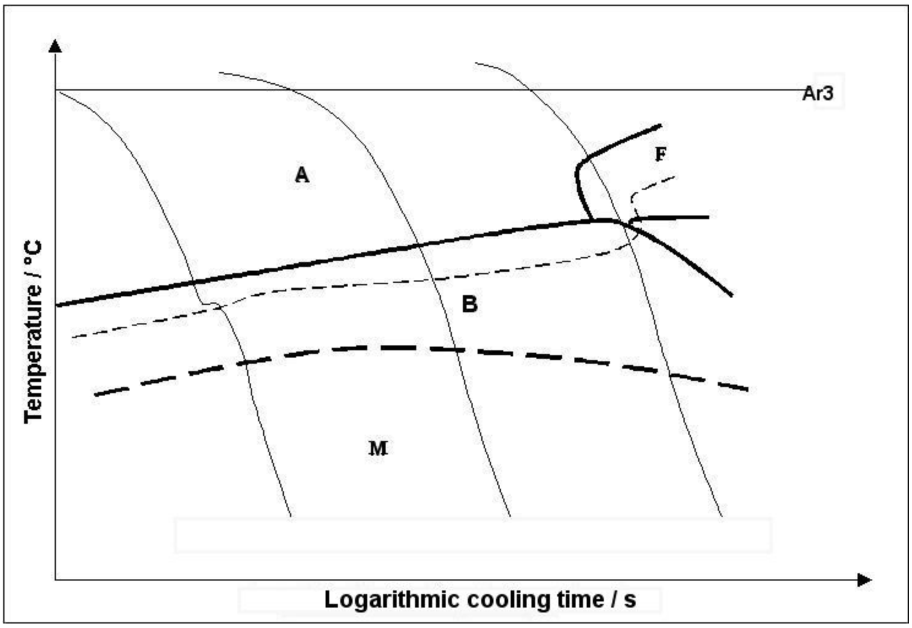

Fig. 1: TTT-diagramme of the presented B-alloyed pipeline steel

A very positive effect of retarding the austenite to ferrite transformation can be found in the widening of the production window for bainitic steels. A bainitic microstructure and therefore the best possible combination of strength and toughness properties can be produced even if the finishing rolling process is carried out at relatively low temperatures. With respect to an optimum combination of the mechanical-technological properties of the product, the formation of martensite has to be avoided [3,6]. **Table 2** summarises the main process parameters for the mill trials of this investigation.

Table 2: Process parameters of mill rolling trials

Parameter	Abbreviation	Value
Reheating Temperature	TR	High, low, ΔTR=90 K
Finish rolling temperature	FRT	≈ Ar3, < Ar3, > Ar3
Cooling rate	CR	10-15 °C/s

Rolling at low temperatures is possible because very little ferrite forms below the Ar3 temperature and therefore no structural changes are to be expected.

During the investigation the influence of different reheating temperatures on the properties of the new steel have been investigated. The choice of an optimum reheating temperature is influenced by the contents of carbon and niobium in the chemical composition. The grain coarsening of austenite during the reheating process is influenced by the time of reheating and the reheating temperature itself. Lowering the reheating temperature on the one hand reduces the initial grain size of austenite which positively influences the toughness properties of the product. On the other hand the reheating temperature must be sufficiently high enough for a maximum dissolution of niobium which forms carbonitride precipitates during the thermomechanical rolling process [7, 8]. The proper balance between lowering the reheating temperature to avoid too high grain coarsening and increasing the reheating temperature for the solution of the micro-alloying elements was one challenge during this investigation.

Due to the strong transformation retarding effect of boron as a micro-alloying element, the finish rolling temperature as well can be decreased. Micro-alloying with less than 40 ppm boron reduces the Ar3 transition temperature by up to 50 °C compared to conventional NbTi micro-alloyed steels.

As the avoidance of martensite in the microstructure is very important to ensure the best possible toughness level in combination with a high strength grade, the cooling stop temperature has to be controlled very carefully. On the other hand a too high cooling stop temperature leads to an upper bainitic microstructure that is also to be avoided [4, 5, 9].

Results

Fig. 2 describes the development of the applied rolling force (dotted line) and rolling temperature (solid line) in the single rolling steps. The slope of the curve for the rolling force exhibits two major points of interest. The first is marked as T_{nr} (recrystallisation stop temperature) and the second one is marked as range of transformation (A_{r3}-A_{r1}).

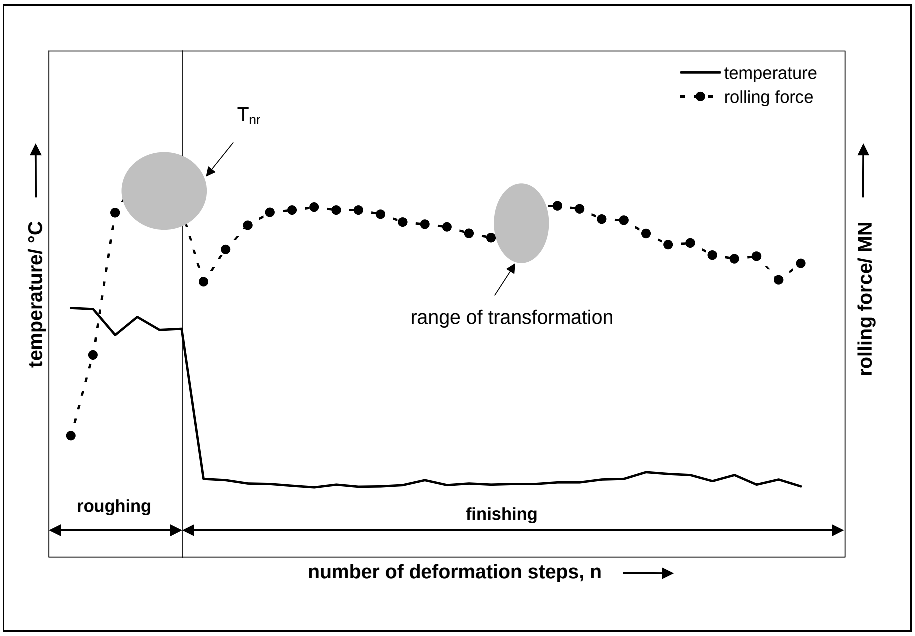

Fig. 2: Applied rolling force and rolling temperature

During pre-rolling the rolling force is steadily increased until it reaches the maximum value in rolling step 4. Afterwards the rolling load remains nearly constant during the last two steps of the pre-rolling phase. This area is marked as T_{nr}.

Between the deformation step number 21 and 22 an increase of rolling force described as range of transformation is observed. These points indicate an important temperature range over which austenite pancaking can be performed during steel rolling. Depending on the chemical composition published algebraic correlations can be used to calculate the specific temperature range. One has to assure that the pre-rolling of the plates is finished before the critical temperature T_{nr} is reached. Below this temperature no recrystallisation takes place and the intermediate product does not have the desired microstructure for the finish rolling step [10].

If the rolling parameters are chosen according to the before mentioned aspects a microstructure as it can be seen in **Fig. 3** is obtained. The microstructure is mainly bainitic and contains only small amounts of ferrite and martensite.

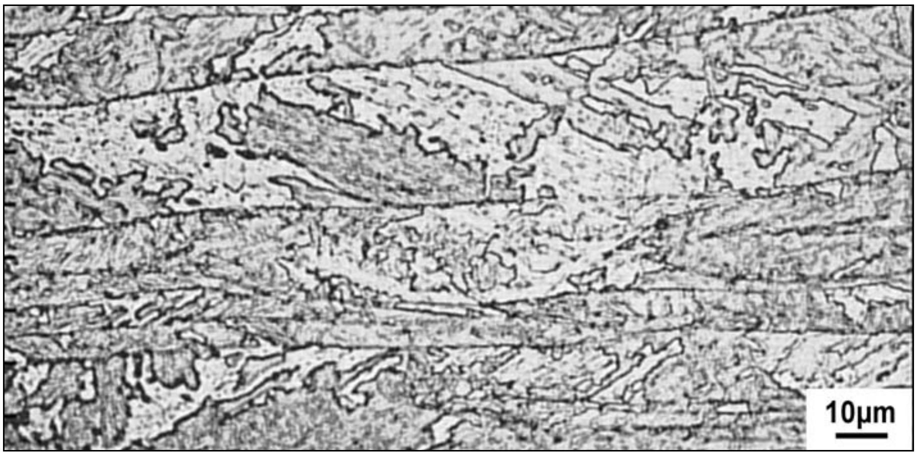

Fig. 3: Typical microstructure of the investigated steel

Fig. 4 gives an overview of the obtained mechanical properties of the rolled plates. As it can be seen from this figure all plates met the required yield and tensile strengths for API grade X80. Some of the plates with the higher reheating temperature even reached yield and tensile strengths in the range of API grade X100. By comparing the results of the two reheating conditions it can be seen that increasing the reheating temperature leads to ~50 MPa higher strength values.

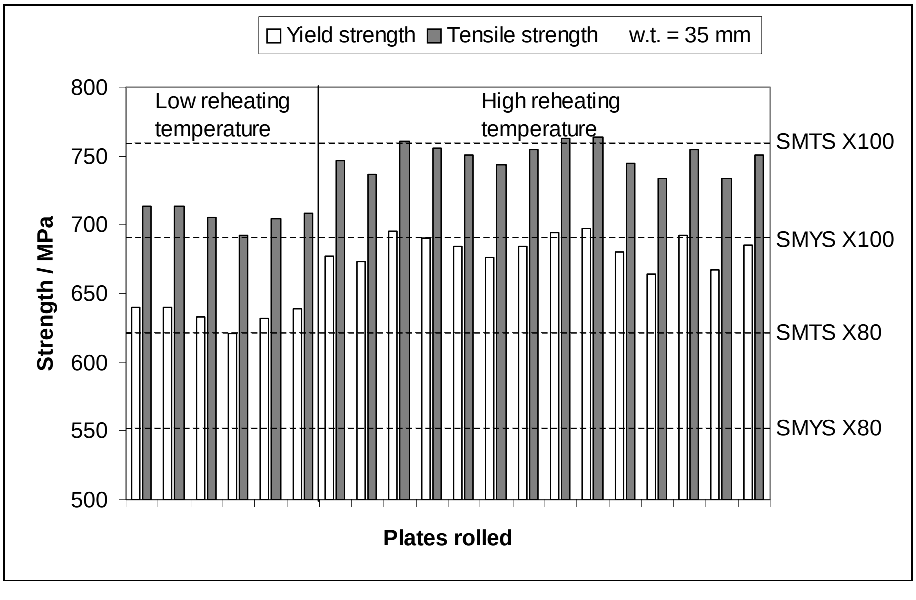

Fig. 4: Yield and tensile strength

Keeping the very low carbon content in mind as well as the fact that apart from molybdenum no other alloying element was used these results underline not only the importance of the thermomechanical rolling process but also the strong influence of boron as a micro-alloying element. The mechanical properties of these steels are very sensitive to the amount of boron added. It is crucial that the boron level in the steel is tightly controlled since it has been shown in previous literature that coarse iron boron-carbides can form above a certain boron level for a plain NbTiB steel. As mentioned before, these precipitates lead to a deterioration of the attainable toughness properties [3].

In **Fig. 5** the results of the Charpy impact tests and the BDWT-tests for all plates are presented. The testing temperature was –20 °C. The plates with lower reheating temperature had impact energy values among 120 J and 210 J while the plates with the higher reheating temperature showed impact energy values between 150 J and 220 J. Low BDWT results between 20 and 65% were obtained at the lower reheating temperature. By increasing the reheating temperature it was possible to increase the BDWT values. Further optimisation of the rolling parameters lead to an additional increase of the BDWT values. The last trials showed a stable BDWT-level above 70% shear area. Due to the lower deformation ratio the roughing phase of the rolling process during which the austenite is forced to recrystallise is less pronounced for a wall thickness of 35 mm [5, 11].

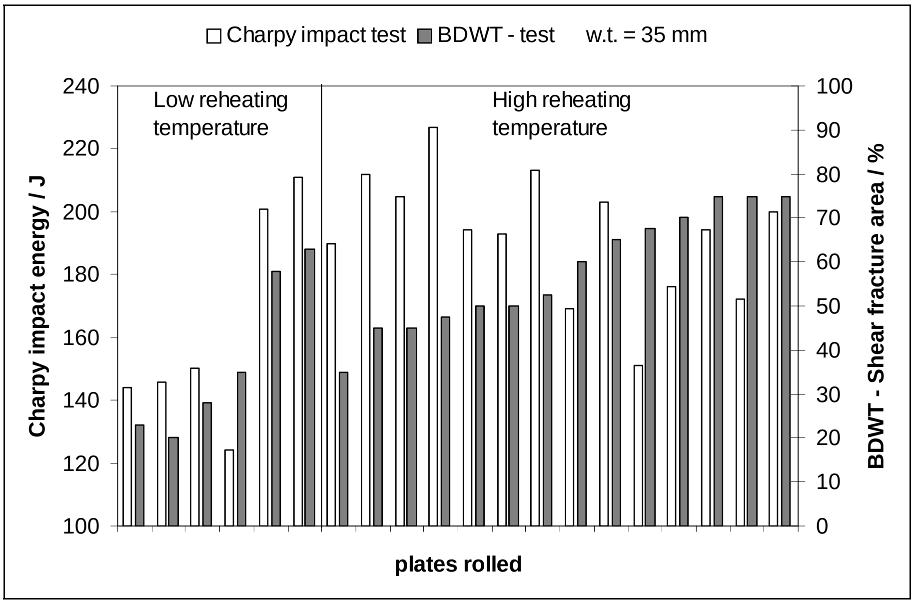

Fig. 5: Charpy impact energy and BDWT – shear fracture area

The already mentioned influence of the reheating temperature on the tensile properties can also be found in **Fig. 6.** An increase of the reheating temperature of about 90 °C causes an enhancement of yield strength and tensile strength. The minimum increase of yield strength found within this investigation was about 20 MPa. For tensile strength a minimum increase of 30 MPa was determined. As illustrated by **Fig. 7** the yield strength was not affected by the time between roughing and finishing. Over a wide range of time spans no evidence for any recovery or softening behaviour was observed.

Depending on the specific chemical composition the reheating temperature has to be high enough to complete the roughing phase of the rolling process before the recrystallisation of the austenite stops. As can be seen from **Fig. 8** a finish temperature for roughing below the recrystallisation temperature of the austenite drastically affects the toughness properties, especially the results of the Battelle drop weight tear test, as the critical grain refinement of austenite during roughing is not achieved.

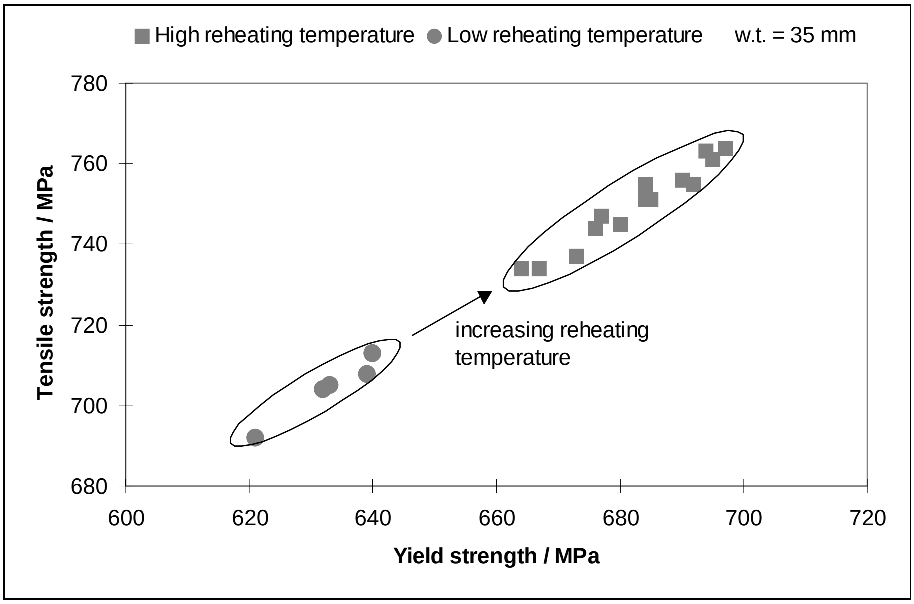

Fig. 6: Influence of reheating temperature on strength properties

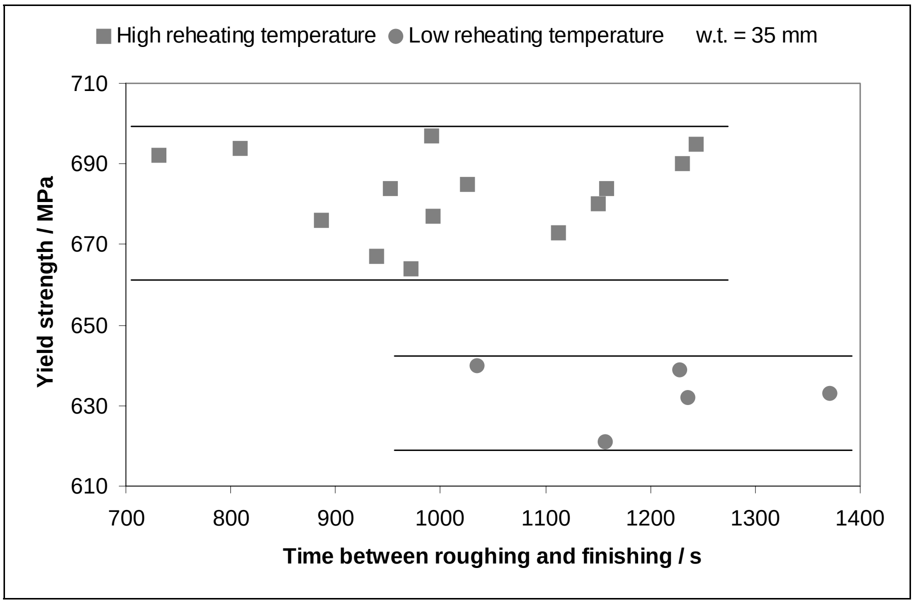

Fig. 7: Influence of the interpass time on the yield strength

The Charpy impact energies decreased with increasing time as shown in **Fig. 9**. When the time between roughing and finishing was almost doubled the determined Charpy impact energies were decreased about 90 J. Lowering the finish rolling temperature to mark the possible process boundaries can drastically increase the time between roughing and finish rolling. This not only negatively affects the productivity of a heavy plate mill, but as well the properties of the product.

Fig. 10 describes the influence of the finish rolling temperature on the Charpy toughness properties. It can be seen here that the upper boundary of the single values is raised while the lower boundary is unaffected to a large extend. When the finishing temperature is increased the lower boundary of the determined values stays nearly unaffected as the upper boundary raises.

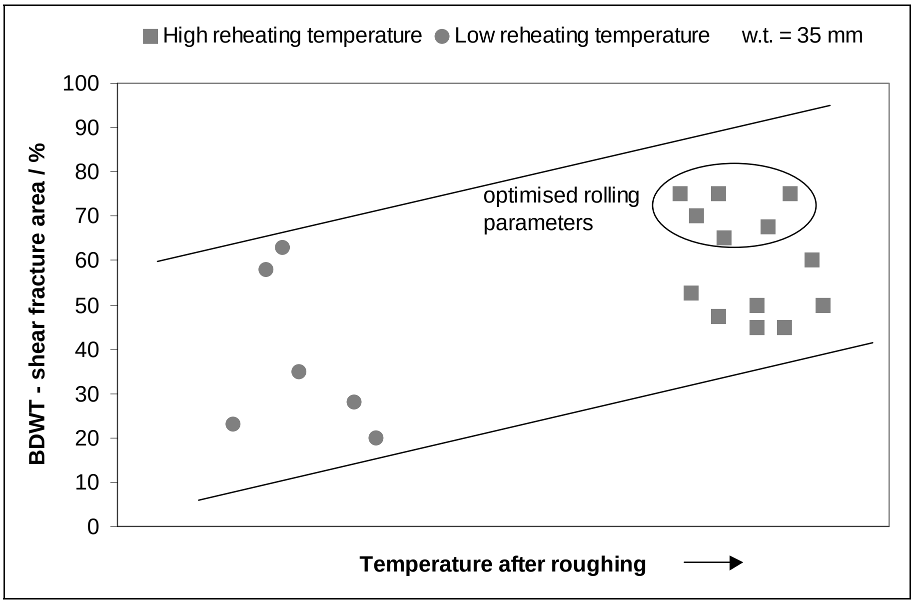

Fig. 8: Influence of the temperature after roughing on the BDWT–results

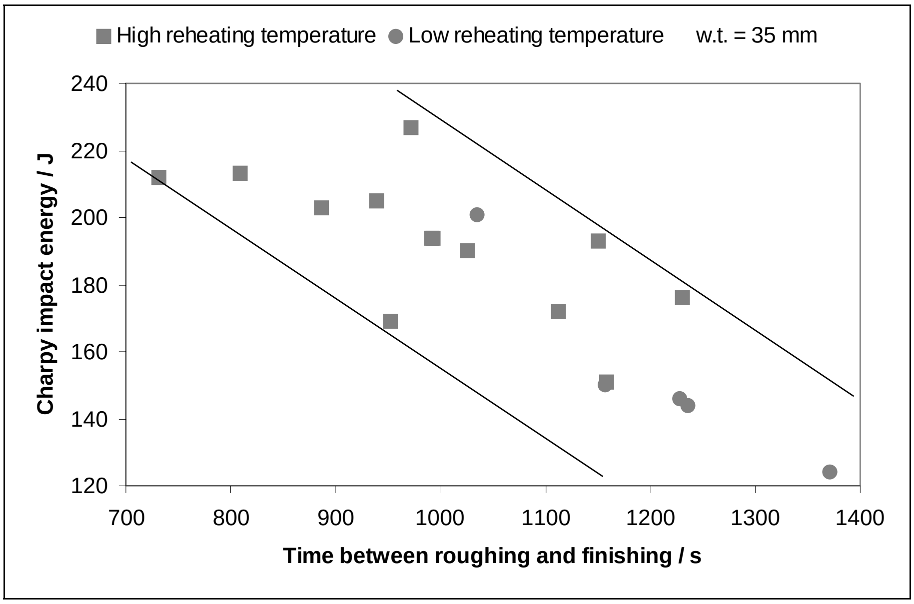

Fig. 9: Influence of the interpass time on the Charpy impact energy

Conclusion

In this paper the results of a large scale mill trial investigation on a low carbon NbTiB micro-alloyed steel are presented. It was observed that for the proper processing of this steel by a thermomechanical treatment each and every individual process parameter has to be controlled and optimised.

The slab reheating temperature influences the strength as well as the Charpy impact toughness properties of the heavy plate material. By increasing the reheating temperature more niobium will be in solution. This positively affects yield and tensile strength. Furthermore, by optimising the reheating temperature and rolling parameters a BDWT level above 70% could be obtained. It can also be assured that the important first or roughing rolling is carried out in the correct range of temperatures above the recrystallisation stop temperature for austenite. Based on these results it is possible to further optimise the rolling parameters to improve the BDWT results.

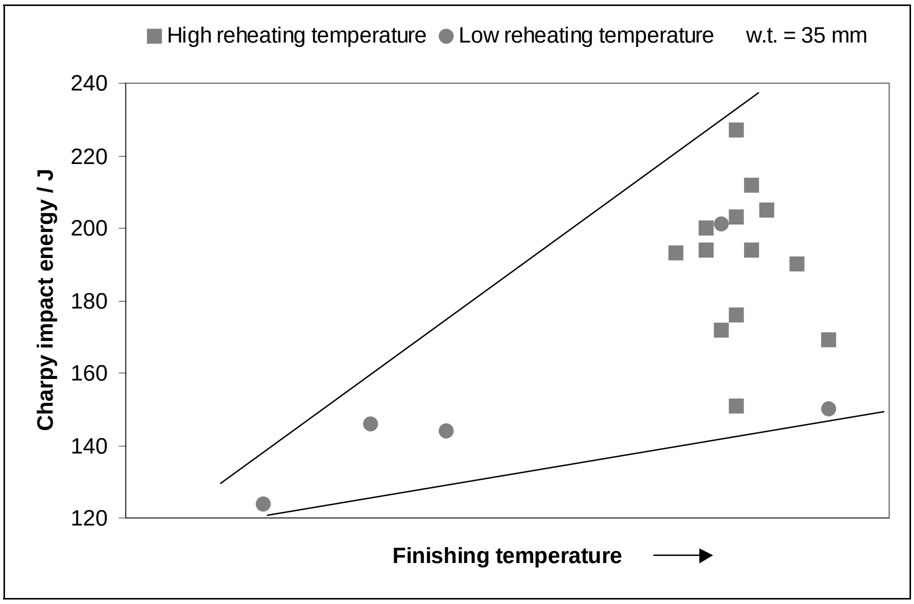

Fig. 10: **Influence of the finishing temperature on the Charpy-results**

Boron causes a shifting of the austenite-ferrite transition curve. Due to this, a bainitic transformation is promoted even at low cooling rates by the addition of small amounts of boron which leads to a wider process window. Due to the bainitic microstructure high and ultra-high strength grades are achievable for a wide range of finish rolling temperatures and even for slow cooling rates.

References

[1] H. Asahi: ISIJ International, Vol. 42 (2002), No. 10, pp. 1150-1155

[2] T. Hara et al.: ISIJ International, Vol. 44 (2004), No. 8, pp. 1431-1440

[3] A. Kern et al.: Thyssen Technische Berichte (1990), No. 1, pp. 43-52

[4] C. J. Heckmann et al.: Proc. of the 2nd Int. Conf. on TMP of Steels (2004), pp. 311-318

[5] S.-C. Wang et al.: Materials Science and Engineering, A157 (1992), pp. 29-36

[6] C. Biegus et. al: Steel Research, Vol. 65 (1994), No. 5; pp. 173-177

[7] W. Bleck et al.: Stahl und Eisen, Vol. 117 (1997), No. 4, pp. 39-46

[8] J. Degenkolbe: Thyssen Technische Berichte (1993), No. 1, pp. 19-30

[9] H. K. D. H. Bhadeshia: *Bainite in steels* (IOM Communications, 2nd edition, UK 2001).

[10] J. J. Jonas: Proc. of the 2nd Int. Conf. on TMP of Steels (2004), pp. 35-42

[11] R. Kaspar et al.: Steel Research, Vol. 65 (1994), No. 6; pp. 242-247

MANNESMANN
RÖHRENWERKE
Ein Unternehmen der Salzgitter Gruppe
Mannesmannröhren Mülheim

Mannesmannröhren Mülheim GmbH, Wiesenstraße 36, 45473 Mülheim an der Ruhr, Germany
Tel. ++49 (0) 208 / 458-04, Fax ++49 (0) 208 / 458-1912
www.mannesmann-mrm.de, email: info.service@mannesmann-mrm.de